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DEVELOPMENT OF NOVEL FLAME RETARDANTS FOR POLYURETHANE FOAMS

by

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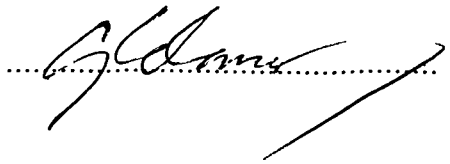
Declaration

Unless otherwise stated, the work in this thesis is that of the author, and has not previously been submitted in part or whole, at this or any other university.



G.V. Coleman B. Sc.(Hons)

ABSTRACT

Development Of Novel Flame Retardants For Polyurethane Foams

In line with current environmental concerns, a non–halogenated, high phosphorus content flame retardant for polyurethane foams is preferred. Cyclic phosphorus compounds have a high percentage of phosphorus and should therefore exhibit good flame retardant activity when incorporated into polyurethane foams. One such group of compounds, known as phospholenes, had previously been successfully synthesised but in poor yields and with only a few derivatives being prepared. This work was concerned with identifying and then optimising synthesis routes to a variety of model phospholene oxide esters, that were proposed to have potential as novel flame retardants. Kinetic and mechanistic studies of the simplest synthesis reaction were also investigated. Once optimisation of both stages of the two stage synthesis were successful in raising the yields from ~25% to >90%, a flow reactor was designed and constructed to facilitate production of the model compounds in large quantities (~1/2 kg) required and then incorporated into polyurethane foams at a variety of loadings. These flame retarded polyurethane foams were prepared and extensive flammability tests were subsequently performed to fully evaluate the model compounds' performance as flame retardants. The model compounds exhibited favourable flame retardant properties, but their physical properties prohibited their use as commercial flame retardants. However the work completed has shown the potential, within this area of compounds, for the commercial development of suitable flame retardants.

To Nig And The Old Alpha,

The People's Labourer Has Done It Again.

"It's At Times Like This, That I Really Wish I'd Listened To What My Mother Use To Say When I Was Young."

'What Was That ?'

"I Don't Know, I Didn't Listen."

Objective

Fire was perhaps the first advancement made by man. Since its discovery, fire has proved to be a major benefit to mankind. Yet the baneful aspects of fire are ever present and have never been successfully eliminated. Uncontrolled fire, possessing enormous destructive capabilities and no conscience, knows no boundaries and takes an ever increasing toll in human suffering and loss of property each year. Social and political pressures are constantly forcing changes in flammability regulations, demanding that effective fire defence keep pace with the growth of new building and transport technology and environmental concerns. Some of the most effective flame retardants contain a high percentage of phosphorus and the most efficient contain halogens as well. It is now understood that the presence of halogens in flame retardants constitute an unacceptable environmental hazard. Due to a general consensus among scientists and politicians, which forced changes in the current environmental legislation, there is an important need for successful and "*environmentally friendly*" flame retardants, in particular, those that do not contain halogens.

The family of compounds known as phospholene oxides, are one such potential flame retardant alternative to the currently available halogenated flame retardants, in particular for polyurethane foams. The aim of this work was to develop a high yield synthetic route for those compounds. A full investigation of their flame retardant properties could then be carried out with reference to a small number of model compounds. Current flame retardants for flexible polyurethane foams are halogenated, there being only a few non–halogenated flame retardants available for rigid polyurethane foams. The test material for flammability studies was chosen as flexible and rigid polyurethane foams, as this class of materials

is already under examination as a consequence of the impending ban on chlorofluorocarbons (CFC's) which are used in their manufacture as blowing agents. The first foam to meet both of these stringent requirements, that is no CFC's used in manufacture and no halogens included in the flame retardant would be a significant breakthrough.

To be successful, the target compound must impart acceptable flame retardant performance and suitable physical properties to the polyurethane foam. The synthesis route must also be straightforward and most of all, economically viable, that is a very high yield $\geq$ 90%.

1.0 Introduction

The atmosphere provides the earth with protection from solar radiation. In particular the ozone layer keeps the ultra violet rays within manageable levels. As a result of the Montreal Protocol [Kemp, D.D. 1990], the use of chemicals that possess the potential to deplete the Ozone layer are being gradually phased out. A complete ban of these chemicals, the majority being chlorofluorocarbons, generally termed "CFC's", is to be enforced by the year 2000. However, due to the persistent stability of CFC's in the environment, their effects upon the ozone layer may continue to be detected for a minimum of 20 — 30 years after production and use ceases totally. The CFC controversy and the extent to which it is responsible for ozone depletion remains in dispute. This reflects society's inadequate knowledge of the workings of the earth/atmosphere system in general, and the photochemistry of the earth's stratosphere in particular. The facts are that CFC's can, through chemical catalytic action, destroy ozone in the stratosphere and that a group of British scientists in 1985 [Farman, J.C. *et al* 1985] detected a hole in the ozone layer over the Antarctic, which is increasing, albeit only slightly. These two facts contributed to the speed with which the world's major industrial nations agreed in Montreal in 1987, to take steps to protect the ozone layer, leading to the proscription of that group of chemicals. Eventually, CFC's will no longer be produced, but their effects will linger on until those presently in the atmosphere are gone.

In dealing with the global aspects of the threat to the ozone layer, it is quite clear that although society now has the ability to cause the problem, and may even possess the technology to slow down and reverse it, its understanding of the overall impact on the earth/atmosphere system lags behind. Until that can be changed, the effects of human activities on

the system will often go unrecognised, response to a problem will of necessity be reactive, and the damage done before the problem is identified and analysed may be irreversible. However, it is not the planet which is under threat, but simply mankind's habitat.

The CFC's, sometimes referred to by their trade name, Freon, came to prominence as a result of life–style changes which have occurred since the 1930's. They are used in refrigeration and air–conditioning units but, until recently, their major use was as propellants in aerosol spray cans containing deodorants, hair spray, paint, insect repellent, and a host of other substances. When the energy crisis broke, they were much in demand as foaming agents in the production of polyurethane and polystyrene foams used to improve home insulation. Polymer foams are also included in furniture and car interiors, and, with the growth of the convenience food industry, they have been used in the manufacture of fast food containers and coffee cups. The gases are released into the atmosphere from leaking refrigeration or air–conditioning systems, or sprayed directly from aerosol cans. They can also escape during the manufacture of the polymer foams, and are gradually released as the foams age.

Advantages of CFC's for the listed purposes, include their stability and low toxicity; under normal conditions of temperature and pressure they are inert — that is, they do not combine readily with other chemicals nor are they easily soluble in water. In consequence they remain in the environment relatively unchanged. Over the years, they have gradually accumulated and diffused into the upper atmosphere or stratosphere where they encounter conditions under which they no longer remain inert — conditions which cause them to break down and release by–products which are immensely destructive to the ozone layer.

In 1974, two scientists [Molina, M.J. & Rowland, F.S. 1974] working in the United States on the photochemistry of the stratosphere, came to the conclusion that CFC's however inert they may be at the earth's surface, are highly susceptible to breakdown from the ultraviolet radiation present in the upper atmosphere. They recognised that the photochemical degradation of CFC's (see Figure 1) releases chlorine, which, through catalytic action, has a remarkable capability for destroying ozone.

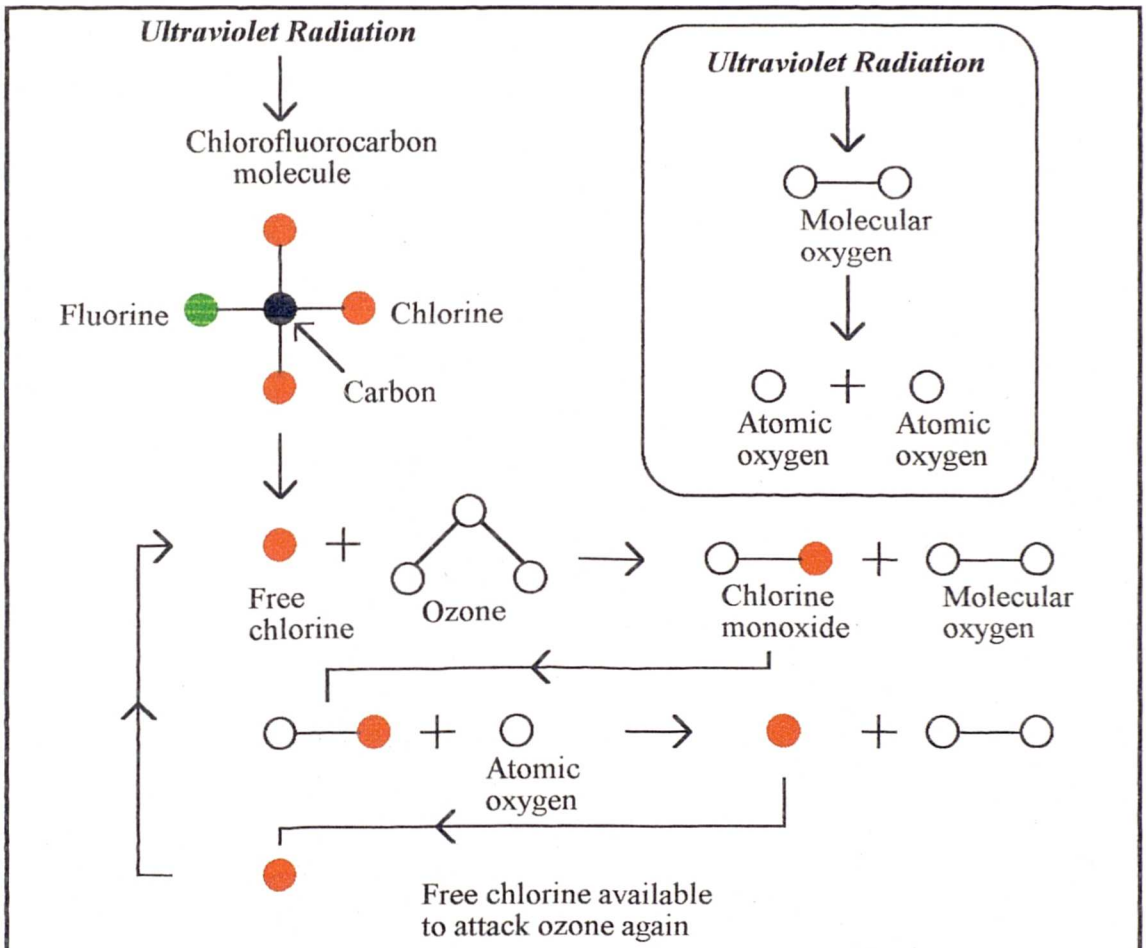


Figure 1 The Breakdown Of A Chlorofluorocarbon (CFC) And Its Effect On Ozone In The Stratosphere

The importance of the chlorine catalytic chain lies in its efficiency; it is six times more efficient catalytically than the nitrogen oxide cycle (another pollutant) for example. The chain is broken only when the free chlorine atom or chlorine monoxide molecule gains a hydrogen atom from the odd hydrogen group, or from a hydrocarbon such as methane, and is converted into hydrogen chloride, which diffuses into the lower atmosphere, eventually to be deposited as acid rain.

The Montreal Protocol also sets strict limitations on the use of certain environmentally hazardous chemicals which may additionally possess an indirect Ozone Depleting Potential (ODP). At the top of the list in this category, are the class of compounds known as "the halogens", the incorporation of bromine into many classes of compounds is now prohibited and chlorine will be the next halogen to be severely restricted in its applications. These restrictions will effectively mean that certain halogens will cease to be a viable chemical to use in industry.

One of the primary uses of halogens in industry today is in the manufacture of flame retardants. Brominated compounds are used to great effect in the flame retardation of a plethora of items e.g. plastics, fabrics, electrical cabinets etc. by Japan. However there is great pressure from European countries to ban their usage, since the incineration of these items at industrial waste disposal sites is known to form dioxins (see Figure 2), a class of non–biodegradeable lethal toxins which are persistent in the environment.

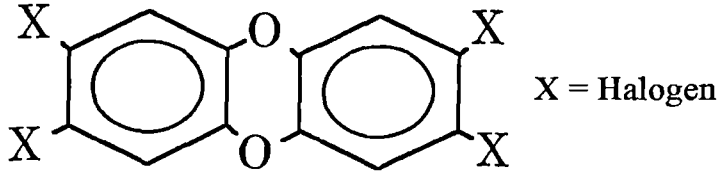


Figure 2 A Dioxin

Chlorinated compounds are used to successfully flame retard almost all items of manufacture from foams to fabrics, plastics to polymers. However chlorine is the next halogen targeted by the current legislation, and the flame retardant industry is actively seeking alternatives to this type of extremely successful flame retardant.

1.1 The History Of Flame Retardants

For over two thousand years mankind has sought methods to reduce the flammability of readily combustible materials. According to the annals of Claudius, the wooden siege towers at the siege of Piraeus in 83 B.C., were protected from fire and flame by treatment with a solution of alum; Aeneas in the fourth century B.C. recommended the use of vinegar to impregnate wood to reduce its combustibility [Ramsbottom, J.E. 1947].

However, treatments for fabrics are of a comparatively more recent date, over three hundred and fifty years ago, in 1638, a treatment of clay and plaster of Paris in the paint, was used on canvas in Parisian theatres, this is the first documented evidence of the use of flame retardants for fabrics [Ward, F. 1955]. Nearly one hundred years later a man named Obadiah Wyld was issued the 551st English Patent in 1735 (the 1st was in 1617) [Conklin, M.N. 1922]. This patent describes the use of "alum, borax, vitriol, or copperas" for flame proofing paper pulp or textiles. The Montgolfier brothers, inventors of the lighter-than-air balloon in 1783, are said to have used similar substances in the coatings of their early models, to reduce the fire hazard. In 1820, King Louis XVIII commissioned Gay Lussac to look into means of protecting fabrics used in the theatre, after some previous personal experiences in Europe with theatre fires. Gay Lussac concluded that out of a variety of substances, ammonium salts of sulphuric, hydrochloric, or phosphoric acid were effective on kemp and

linen fabric and noted improvement by using a mixture of ammonium chloride and ammonium phosphate. This early work still remains valid and applicable today, having withstood the scrutiny of all subsequent workers.

At the turn of the century flannelette became a cause for concern because of its extreme flammability. This led to the renowned chemist William Henry Perkin becoming involved in the problem of flame retarding fabrics. He defined the requirements for a flame proofing process in words that are still satisfactory today as they were in 1913 :

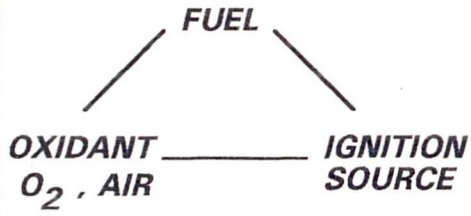
A process, to be successful, must, in the first place, not damage the feel or durability of the cloth or cause it to go damp as so many chemicals do, and it must not make it dusty. It must not affect the colours or the design woven into the cloth or dyed or printed upon it; nothing (such as arsenic, antimony, or lead) of a poisonous nature or in any way deleterious to the skin may be used and the fireproofing must be permanent, that is to say, it must not be removed even in the case of a garment which may possibly be washed 50 times or more. Furthermore, in order that it may have a wide application, the process must be cheap [Perkin, W.H. 1913].

Perkin's research validated the data obtained by Gay Lussac and others [Hunt, W.H. 1910] and led to a commercial process called "Non–Flam." This process involved impregnating the flannelette with sodium stannate and then ammonium sulphate, followed by washing and drying. However his process did not win popular favour [Ward, F. 1955] and little more was done on flame proofing until the outbreak of World War II [Chase, W.W. 1943]. it was during the late 1930's and early 1940's that waterproof and flame proof canvas was developed for outdoor use by the military.

Since the end of World War II the search for more durable and successful flame retardants has continued at an ever increasing pace. Consequently, the majority of the total literature has appeared since then.

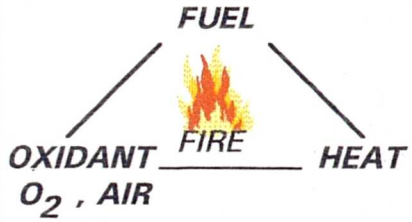
1.2 Mode Of Action Of Flame Retardants [Kuryla, W.C. 1979]

In order to understand the action of flame retardants one must first be aware of what occurs during combustion and where the flame retardant action can impinge. In basic terms one can imagine that a *Fire Triangle* exists, see Figures 3a & 3b.



In order to prevent a fire the fire triangle must be broken i.e. prevent oxidant getting to the fuel or ensure there is no ignition source.

Figure 3a Fire Triangle :— Ignition



To control or stop the fire, either heat or oxidant must be prevented from reaching the fuel.

Figure 3b Fire Triangle :— Sustained Combustion

For solids undergoing combustion e.g. polymers, their behaviour can be adequately summarised by the polymer combustion cycle [Price, D. 1987], see Figure 4. In this diagram, the polymer is subjected to a heat source which raises the polymer's temperature. When the temperature is high enough, thermal decomposition occurs and fuel is evolved. Ignition

occurs if the pyrolysis temperature of the polymer exceeds the polymer's ignition temperature. This degradation generates combustible gases which mix with oxygen and then burn in the flame zone. This flaming combustion consumes oxygen from the air and produces smoke, fumes and more heat. If some or all of the heat generated is returned to the polymer then further pyrolysis of the polymer is promoted, resulting in subsequent evolution of more combustible gases. This then maintains the combustion cycle if sufficient oxygen and evolved combustible gases are available and so the process becomes self sustaining.

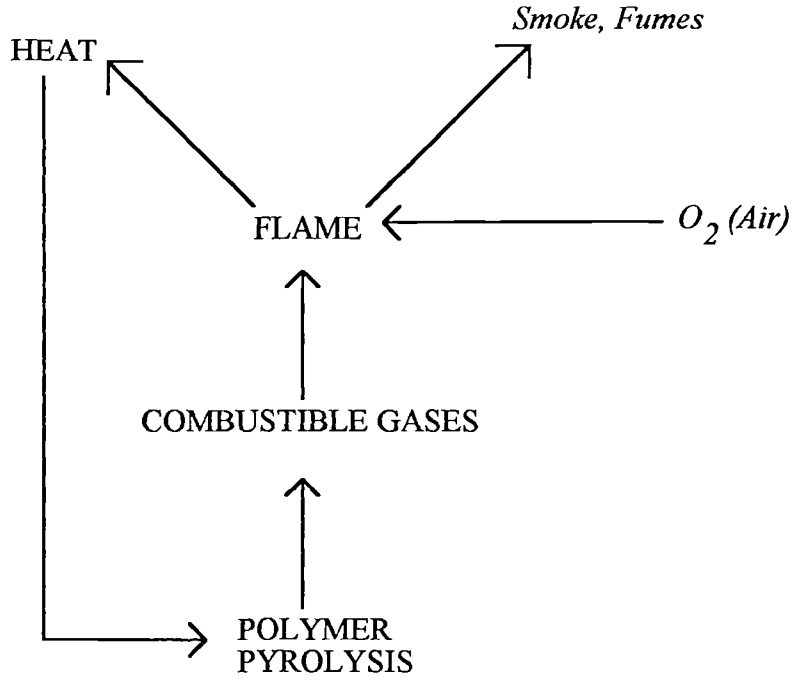


Figure 4 The Self Sustaining Polymer Combustion Cycle

The action of the flame retardant must be to break the combustion cycle either physically, chemically or by a combination of the two [Barker, R.H. 1979]. The net effect is :—

a) a reduction in the heat input to the polymer.

b) the removal of flammable volatiles i.e. the '*fuel*', from the flame.

c) prevention of oxygen access and or dilution of the flame.

d) raising pyrolysis temperature.

e) raising of temperature of ignition of combustibles and or interference with flame chemistry.

The primary activity of the principal flame retardant agents are in one of two phases, either the condensed (liquid) phase or the vapour (gas) phase, see Figure 5. Fire retardants can operate not in one single mode but collectively over several modes. They are therefore classified according to which phase of the combustion process they are most effective in. In addition, the inherent behaviour of a polymer to a flame however, can be more effective than the fire retardant activity, such properties cause melting/dripping of the polymer away from the combustion zone. This

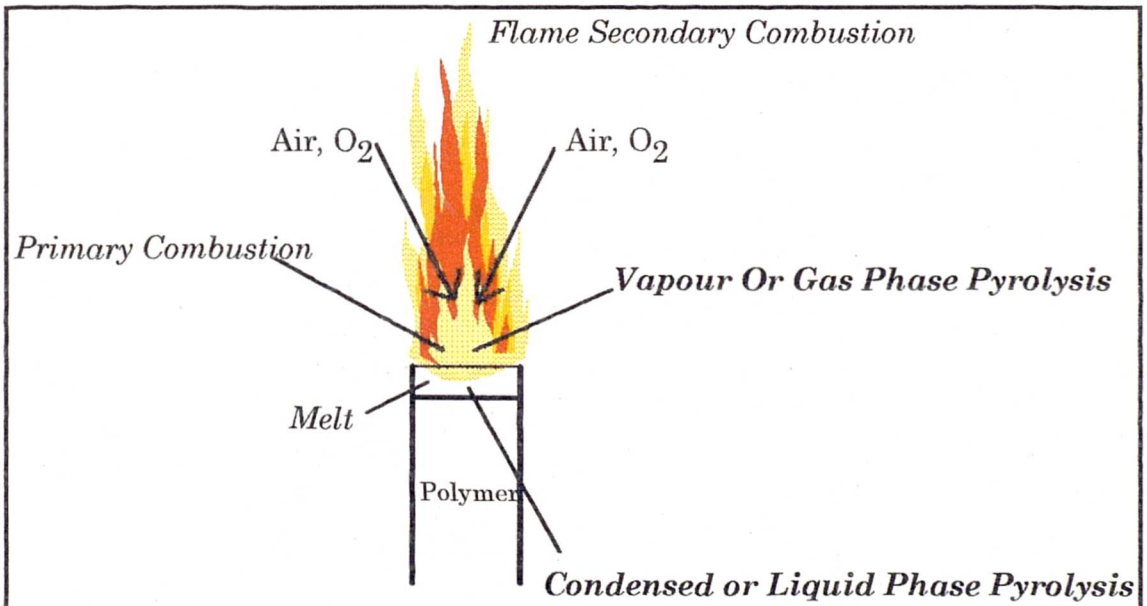


Figure 5 Combustion And Pyrolysis Phases

action removes the polymer from the flame zone and combustion ceases as the fire triangle is broken. Examples of this type of polymer are polythene, polyester etc.

1.3 Vapour Or Gas Phase Activity Of Flame Retardants

Vapour phase flame retardants are effective for reducing the flammability of most organic polymeric materials since they interfere with the similar flame chemistries [Hastie, J.W. 1973]. As mentioned before the activity can be either physical or chemical in nature or a combination of both.

1.3.1 Physical

Physical activity can take the form of an additive which when subjected to a heat source will decompose to release a non–flammable gas. This non–flammmable gas acts as a dilutent to the flammable volatile gases. The effect of such dilution are two fold :—

i) it decreases the rate of combustion,

ii) it increases the amount of gas to be heated by the flame, therefore resulting in a lower flame temperature.

An example of this type of additive is aluminium trihydroxide (generally termed ATH) : —

$$Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

The water evolved on heating aluminium hydroxide acts as a dilutent in the flame.

1.3.2 Chemical

Chemical activity is naturally more complex than physical activity and attempts to inhibit the complex flame chemistry of combustion [Tesoro, G.C. 1978]. Combustion can be thought of as a branching chain process involving simple radicals, arising from the polymer undergoing pyrolysis. This branching chain process is propagated by $H\cdot$, $OH\cdot$, $HO_2\cdot$ radical species. Halogen acids (HX) inhibit this combustion process via :—

$H\cdot + HX \rightarrow H_2 + X\cdot$ and $OH\cdot + HX \rightarrow H_2O + X\cdot$

Where $X\cdot$ = Bromine or Chlorine radical, which are less reactive than $H\cdot$ and $OH\cdot$.

Halogen acid 'mops up' chain propagating radical species, generating chain terminating halogen radicals, which re–propagate the halogen acid via :—

$X\cdot + RH \rightarrow R\cdot + HX$ RH = *Fuel*, generated from the polymer.

It is important that the decomposition temperature of the flame retardant occurs just before that of the polymer, so that the combustion inhibiting HX species are present when the polymer vapours reach ignition temperature. Normally decomposition temperature of the flame retardant is 50°C lower than that of the polymer. Bromine is a more efficient radical inhibitor than chlorine and is usually introduced in the form $C_nH_{2n}Br$. However, as mentioned previously, the use of brominated flame retardants is banned in certain countries, as the burning of items containing brominated flame retardants in waste incinerators, produces

dioxins. Examples of this type of flame retardant are halogenated aromatic/aliphatic compounds, e.g. Amgard V200 (Albright & Wilson) and polybrominated diphenyl ethers.

Also included in this category of gas phase retardants are certain combinations of chemical compounds which exhibit the phenomenon known as synergy, that is the effect produced by combining the actions of two chemicals is greater than the sum of their individual effects when in isolation. An example of this type of flame retardant is the metal oxide / halogen compound combination, such as the well known Antimony (III) Oxide / Aliphatic Bromide combination. This not only provides the flame inhibition properties of HBr but also the radical removal by reaction at the surface of SbO particles, the so called 'wall effect'. The interesting fact is that the combined effect of these two actions is significantly greater than the sum of the flame retardant effects of the oxide and bromide when used in isolation [Weil, E.D. 1975].

1.4 Condensed Phase Activity Of Flame Retardants

As was the case with vapour phase active flame retardants, condensed phase flame retardants can function in either a physical or chemical manner, or a combination of both. However unlike vapour phase flame retardants, condensed phase flame retardants only operate on individual polymeric substances with whose pyrolysis mechanisms they can interact [Barker, R.H. 1979]. This restricts their use e.g. Proban 210 (Albright & Wilson) only functions effectively on cellulose.

1.4.1 Physical

The physical action of condensed phase flame retardants is to act as either fillers which increase the polymer's heat capacity or as intumescent additives which decompose endothermically to form an intumescent barrier [Kuryla, W.C. 1978], see Figure 6.

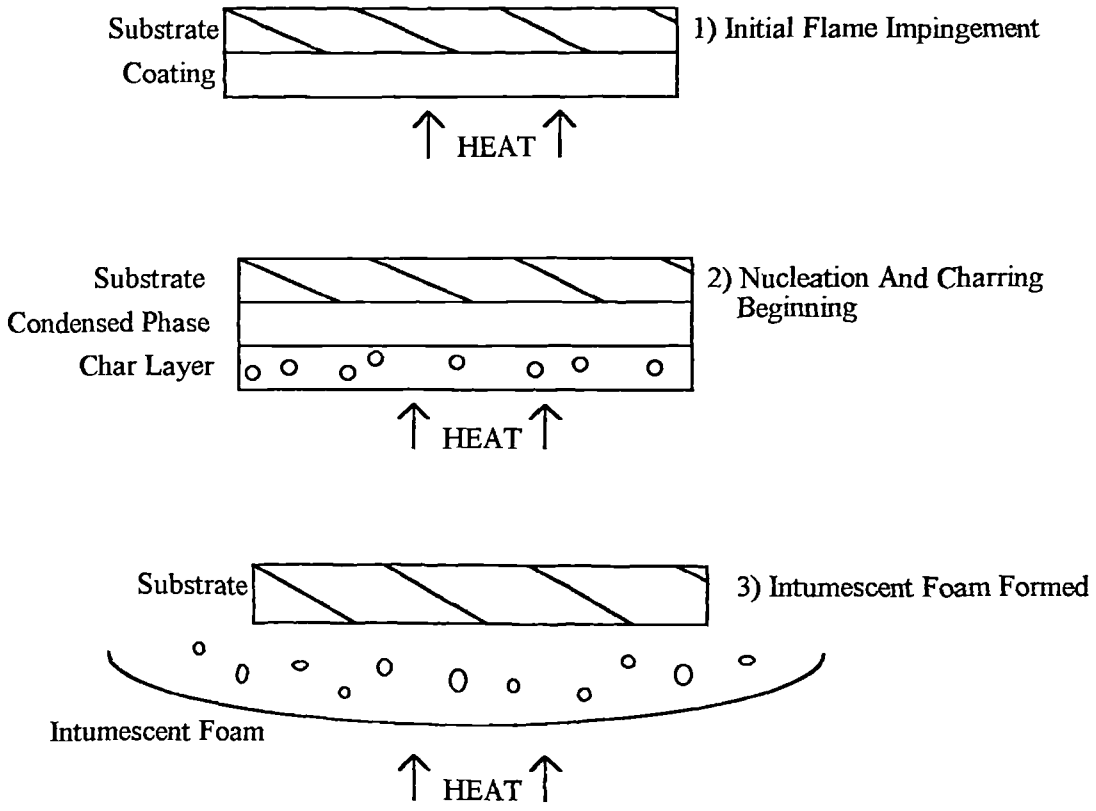


Figure 6 Formation Of An Intumescent Barrier

Intumescent flame retardants are normally applied as a coating consisting of three components :—

i) an intumescent catalyst (inorganic precursor) which decomposes between 100°C and 250°C to form a strong inorganic acid to act as a dehydrating agent.

ii) a carbonific compound (hydroxlated carbon compound) which is dehydrated by the strong inorganic acid to form char.

iii) A spumific compound (or blowing agent) which yields a non–flammable gas on heating, causing the char to bubble and form a thick insulating coating.

Examples for this type of composite flame retardant are i) dihydrogen ammonium phosphate, ii) any monomeric or polymeric carbon compound, e.g. pentaerythritol, iii) dicyandiamide or chlorinated polymers.

In order to secure intumescence with these ingredients, four important steps must occur in precise order.

1) The intumescent catalyst must decompose to form the acid catalyst. In the case of dihydrogen ammonium phosphate, the acid is phosphoric acid.

$$NH_4H_2PO_4 \xrightarrow{\Delta} NH_3 + H_3PO_4$$

2) Phosphoric acid reacts with the carbonific compound (pentaerythritol) to give a phosphate ester (general formula shown).

$$C_5H_8(OH)_4 + H_3PO_4 \longrightarrow C_5H_8(OH)_4.H_3PO_4$$

3) The phosphate ester decomposes to phosphoric acid, water and a carbonaceous char.

$$C_5H_8(OH)_4.H_3PO_4 \xrightarrow{\Delta} H_2O + H_3PO_4 + C$$

4) The spumific compound (chlorinated paraffin and dicyandiamide) decomposes releasing non–flammable gases which blow the carbonaceous char into an insulative foam protecting the substrate.

$$C_nH_{2n+2}Cl_n \xrightarrow{\Delta} HCl + C$$

$$C_2H_4N_4 \xrightarrow{\Delta} C + NH_3 + N_2$$

1.4.2 Chemical

The chemical action of condensed flame retardants is to decrease the polymer degradation rate by modifying the polymer degradation mechanism hence resulting in a reduction of the fuel available. They can also promote charring which will introduce a barrier effect, reduce the flammable volatiles escaping and give the added benefit that char burns slowly. Examples of this type are phosphonium salt–urea–ammonia cured polycondensates.

1.5 Toxicological Factors

An important factor to bear in mind for any potential flame retardant is its toxicity and behaviour both physically and chemically to fire. All fire atmospheres are potentially lethal and can be classified into a number of significant factors for defining a fire atmosphere from a toxicological point of view.

- the yields of oxides of carbon and reduction in oxygen.

- the concentrations of additional specified toxic gases.
- types and concentrations of unburnt organic products.
- rate of production and total quantities of products of major toxicological significance.

Other important aspects regarding the fire atmosphere include obscurational density and temperature of the atmosphere.

What first appears to be an acceptable flame retardant may unexpectedly increase the danger of a fire atmosphere through its behaviour in a fire situation e.g. by the production of additional specified toxic gases and an increase in the obscurational density of the fire atmosphere.

1.6 The Fire Hazard In The UK

Fire brigades attended 436,000 fires in 1991 [UK Fire Statistics 1991], see Figure 7 for a breakdown according to location, for all fires attended in 1991. The number of fires reported in 1991 was 7% fewer than in 1990, because outdoor fires fell by over 40%. Fires in dwelling increased slightly, accounting for 25% of all the fires attended in 1991. Over the past ten years there has been a steady increase in both vehicle fires and fires in dwellings. The past three years has seen outdoor fires at their highest since 1984 but chimney fires have been decreasing since 1985.

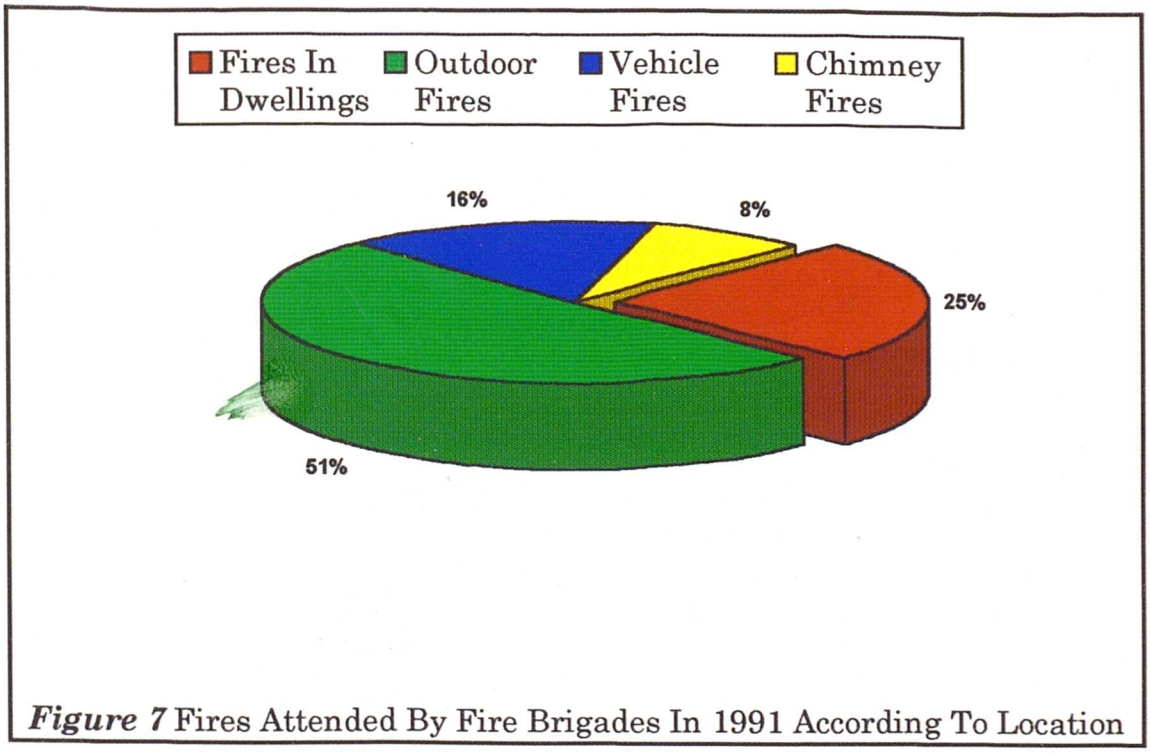


Figure 7 Fires Attended By Fire Brigades In 1991 According To Location

For the 25% of fires in dwellings the most frequent cause of fire was the misuse of equipment or appliances (42%). The total number of annual fire fatalities from all fires has dropped to 816 fatalities, compared to 898 in 1990. Some 608 of the fatal casualties (about 75%) were caused by fires in dwellings. However the number of non–fatal casualties is constantly

increasing each year and was at 14,980 in 1991, with 11,240 (about 75%) caused by fires in dwellings. Figure 8 subdivides the fires in dwellings reported according to material or item first ignited. Fires started by food (primarily fat) being first ignited occupies the largest section, some 35%.

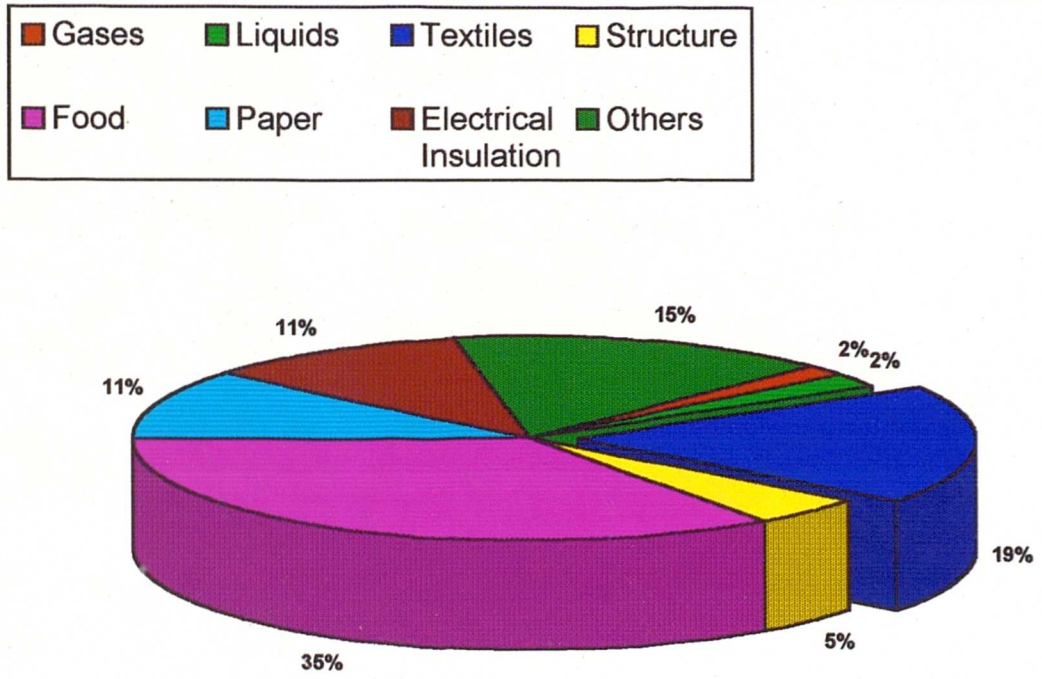


Figure 8 Fires In Dwellings By Material First Ignited 1991

Similarly the non–fatal (see Figure 9) and fatal (see Figure10) casualties from fires in dwellings can be subdivided according to material or item first ignited.

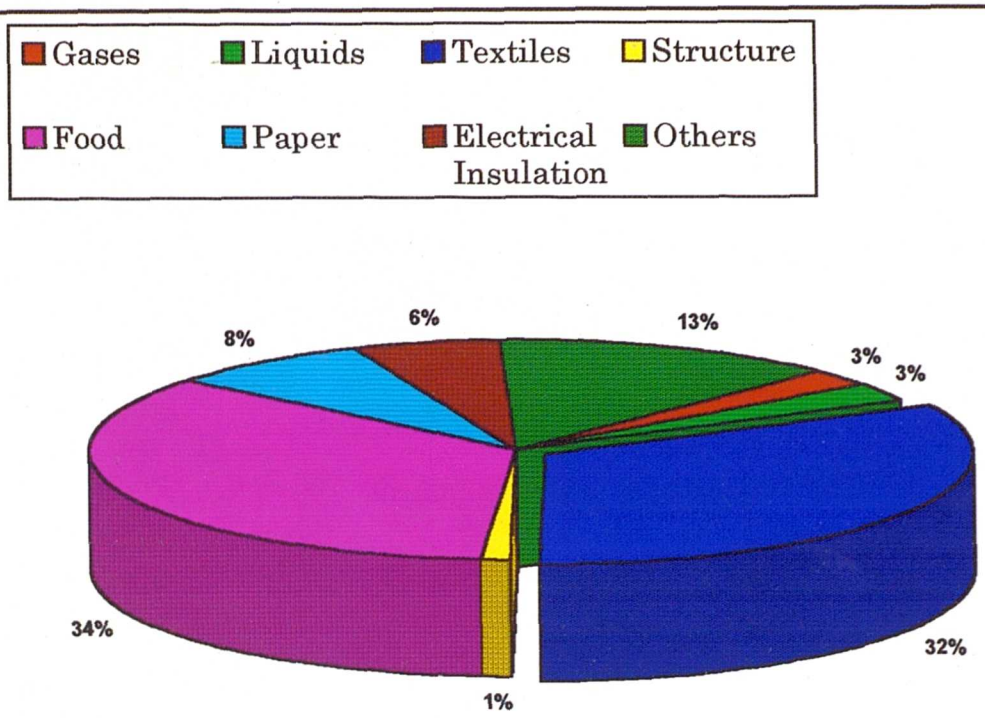


Figure 9 Non–Fatal casualties In Dwellings By Material First Ignited 1991

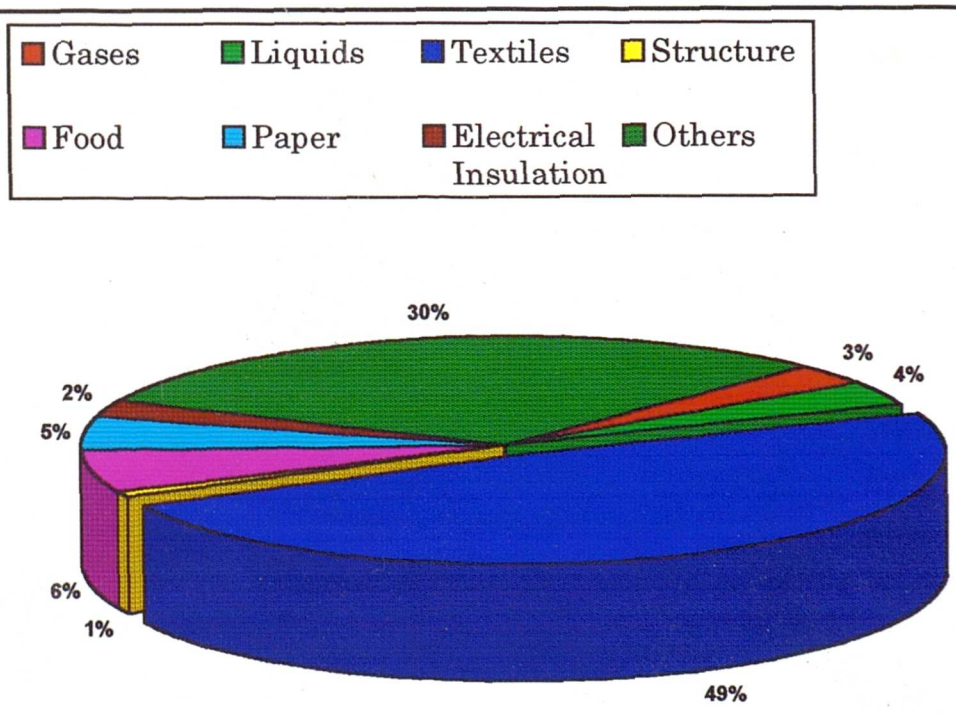


Figure 10 Fatal Casualties In Dwellings By Material First Ignited 1991

Some 32% of non–fatal casualties and 49% of the fatal casualties were caused by textiles and upholstery being the first material ignited. Remembering that this category includes a host of materials, collected under the generic heading of textiles, then, when this category is subdivided further, yet more startling inferences can be seen as shown in Figures 11—13.

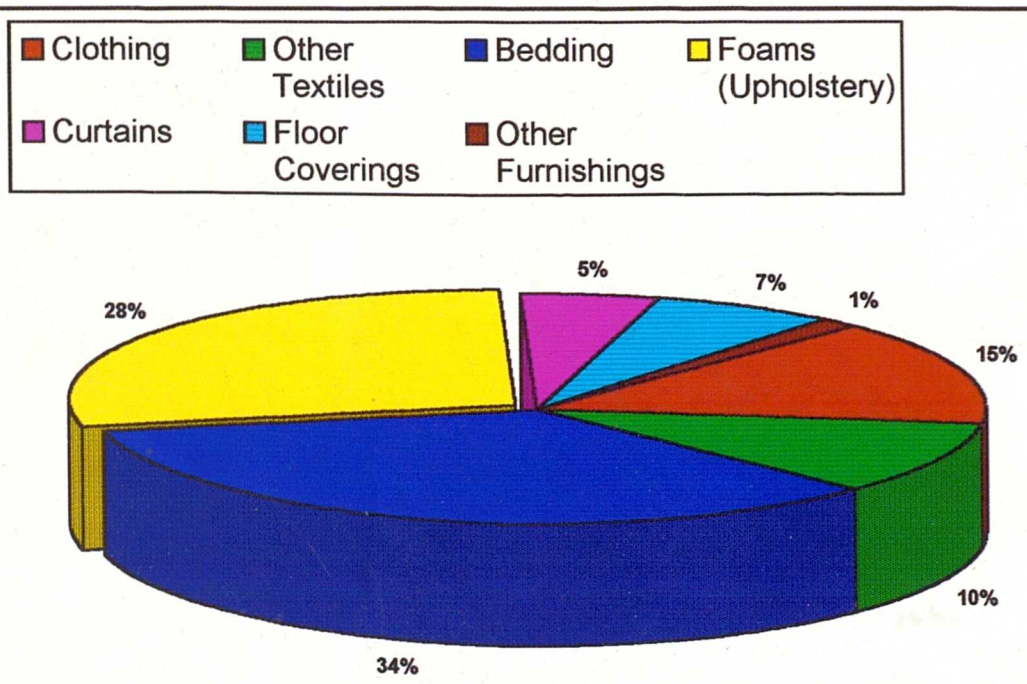


Figure 11 Fires Caused By Different Types Of Textile Material Being First Ignited 1991

Although bedding materials give rise to slightly more fires, foams are responsible for more non–fatal and fatal casualties than any other single material, over 19% of the death toll for fires in dwellings in 1991 (14.5% of total death toll from fires in 1991) and over 13% of the non–fatal casualties (10% of total of non–fatal casualties from fires in 1991). These statistics are for 1991, the most up to date the author could request, prefatory reports indicate that the situation has worsened since then,

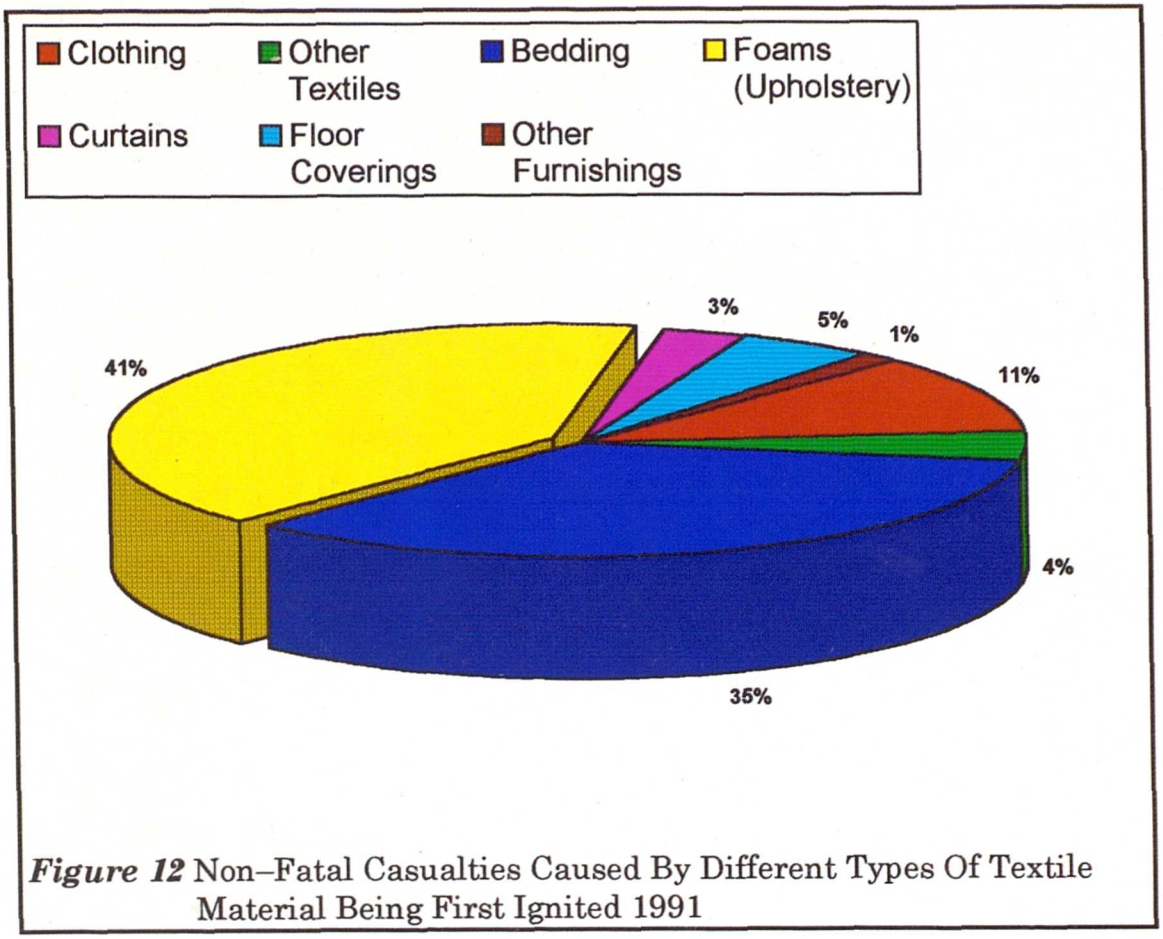


Figure 12 Non–Fatal Casualties Caused By Different Types Of Textile Material Being First Ignited 1991

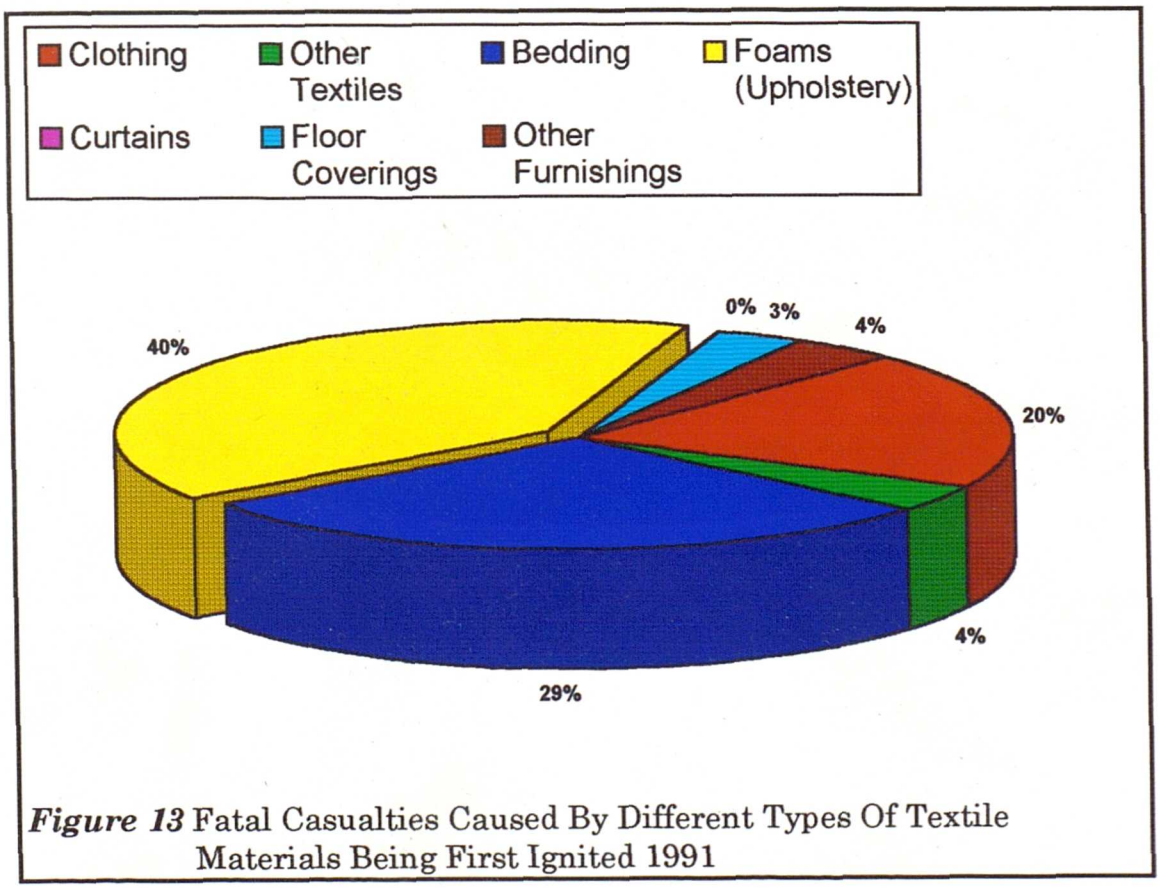
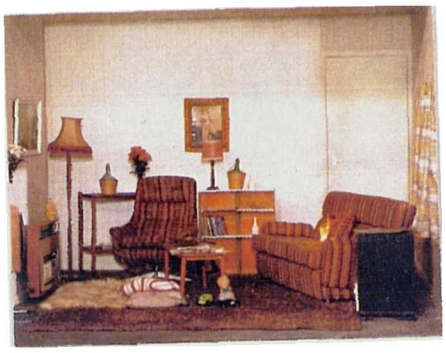


Figure 13 Fatal Casualties Caused By Different Types Of Textile Materials Being First Ignited 1991

following the same trends as seen in 1991.

The need for successful flame retardants for polyurethane foams is therefore apparent, as they are directly responsible for over one quarter of the annual death toll for fires in dwellings. Fires in dwellings (or any enclosed space) behave differently to outdoor fires. Most people are only exposed to garden bonfires and so their conception and understanding is based upon their experiences with bonfires e.g. if the bonfire becomes to hot, taking a few steps back will reduce the radiant intensity. However, within a room the fire can spread rapidly along walls and ceiling and in some cases overtake the escaping people. The ceiling, floor and walls also radiate heat back and so if the fire becomes too hot, taking a few steps back will not dramatically reduce the radiant intensity because the individual is unknowingly subjected to multiple heat sources i.e. from the actual fire and floor, walls and ceiling spreading the fire. In the tragic Bradford football fire in May 1985, the fire in the back of the grandstand spread extremely quickly and was virtually ignored by the spectators in its initial stages. At its height the radiant heat from the fire, to anyone standing at the front of the grandstand (perimeter wall), was sufficient to cause rapid ignition of clothing and multiple burn injuries within seconds [Woolley, D. 1987].

The speed at which a room fire can develop into a major conflagration is one which astounds most people, polyurethane foams within furniture are a major factor in this rapid fire growth. Plate 1 portrays the growth of a room fire started by ignition from a cigarette on the settee.



30 secs After Ignition

1 min 15 secs After Ignition

2 mins 15 secs After Ignition

3 mins After Ignition

3 mins 20 secs After Ignition — FLASHOVER

Plate 1 Room Fire Test

Before the advent of polyurethane foams, room fires took upwards of 10 minutes to achieve flashover, primarily due to the extensive use of wood in the furniture, which in simplistic terms, takes longer to burn. Consumer pressure and a need to reduce costs over the years, has driven manufacturers to produce more comfortable aesthetically pleasing furniture, making extensive use of cheaper alternatives — polyurethanes and other highly flammable materials. However, most importantly, due to the excessive number of domestic fires in 1987, 1988 legislation [Furniture and Furnishing Fire Safety Regulations 1988] banned non–flame retarded polyurethane foams for all new furniture in the U.K. As a consequence industry has had to rapidly switch manufacture formulations to produce Combustion Modified High Resilience polyurethane foams. This was successfully achieved by using halogenated flame retardants.

Now however, the flame retardants currently used for polyurethane foams may soon be banned, due to their halogen content. Therefore it is imperative that successful non–halogenated flame retardants for polyurethane foams be developed. The most widely used element in flame retardant chemistry is phosphorus, a high percentage of phosphorus in the compound being essential to impart favourable flame retardancy. Typically halogenated organic phosphate esters used to flame retard polyurethane foams have 15 – 20% phosphorus content.

1.7 Phosphorus

In the 12th century an Arabian alchemist, named Alchid Bechil, is believed to have isolated phosphorus [Hoefer, F. 1843]. However the actual discovery of the element is attributed to Hennig Brandt, an impoverished merchant seeking to restore his wealth by converting base metals into gold in the year 1669 [Peters, H. 1912]. Whilst conducting his

alchemical experiments with urine, Brandt boiled the urine down to a syrupy consistency and then distilled it after it was amalgamated with sand and charcoal (he could have used practically any phosphorus containing compound e.g. calcium phosphate of bones, as reduction of any phosphorus containing compound will prepare elemental phosphorus). The resulting white liquid residue was elemental phosphorus, thus he had discovered white phosphorus. For many years the manufacture of elemental phosphorus was kept highly secret, even amongst alchemists, because of the mysterious almost magical ability of white phosphorus to glow and burst into flames when exposed to air.

The name phosphorus — from φως, light; φερω, I bear — was first applied to all substances which glowed in the dark but was later restricted to this element, which originally bore such names as phosphorus mirabilis and noctiluca consistens.

The distinction between the chemistry of carbon compounds, organic chemistry, and that of all other compounds and elements, inorganic chemistry, occurred in the middle of the 19th century, when it was shown that urea could be formed from ammonium isocyanate [Wohler, F. 1828]. Before that time, organic chemistry was presumed to cover the chemistry of living things, whilst inorganic chemistry covered inanimate objects. Organic chemistry is characterised by the classification of compounds into a relatively small number of homologous series, and the development of synthetic methods whereby specific complex molecules can be prepared according to previously written structures. Even though family relationships between inorganic compounds are sometimes described, a large group of known inorganic compounds are characterised only by their proximate analysis with their exact atomic arrangement being a mystery. Classical compendia would have us believe that

practically all inorganic compounds are relatively simple structures of low molecular weight.

With the element phosphorus it becomes apparent that there are a number of homologous series in the chemistry of phosphorus and that in many respects the chemistry of phosphorus is quite similar to organic chemistry. The inorganic compounds of phosphorus dominate the commercial application of phosphorus compounds, with the fertiliser industry accounting for about 70% and detergents for 15%. One specific , although small (about 2%) market share is that of organophosphorus chemistry and the heterocyclic derivatives of phosphorus. These are high value added chemicals so that they account for a much greater proportion of the commercial value of the phosphorus industry. A major driving force in the development of organophosphorus chemistry was the recognition of their biochemical properties. This culminated with the discovery of their insecticidal activity and as a spin off from this, the realisation by Germany of their neurotoxicity, where nerve agents were developed for chemical warfare in the Second World War. Fortunately they were never used. Since 1944, hundreds of organophosphorus insecticides have been developed, the attraction being their high toxicity coupled with a limited stability in the biosphere (between 2 and 10 days).

The use of organophosphorus compounds as flame retardants, typically halogenated phosphate esters is even more recent. In the early 1970's, tris(2-chloropropyl)phosphate (TCPP) was marketed as a flame retardant by ICI Ltd and is still in use today. The relatively modern field of heterocyclic chemistry of phosphorus has been growing at a rapid rate since 1970 [Mann, F.G. 1970]. In 1974, a heterocyclic derivative of phosphorus based on a phosphorus containing oligomer, showed flame retardant activity when incorporated into a polymer system [Moedritzer, K. 1974].

The prime objective of the investigations reported in this thesis, was concerned with the search for a suitable heterocyclic derivative of phosphorus for incorporation into polyurethane foam systems as an effective flame retardant.

1.7.1 Flame Retardants Based On Phosphorus

Recalling the work accomplished by Gay Lussac in 1820, the best types of inorganic phosphorus flame retardants were ammonium phosphates. Due to the lack of knowledge about their chemistry at that time organophosphorus compounds were not available for investigation until the mid to late 1940's.

1.7.2 Survey Of Available Phosphorus Flame Retardants [Weil, E.D. 1991]

1.7.2.1 Red Phosphorus

This is a stable and non–toxic form of phosphorus, being a cross linked polymer made by heating yellow phosphorus to a high temperature. Stabilised and coated red phosphorus is in commercial use as an effective flame retardant additive, in Europe in nylon moulding resins, polyethylenes and epoxides [Davies, P.M. 1993]. The red colour can be masked with TiO_2.

1.7.2.2 Ammonium Phosphates — Soluble Salts

Ammonium phosphates are inexpensive effective non–durable flame retardants for paper, non woven disposable goods and

wood. Many commercial applications are available in which ammonium phosphates are blended with ammonium bromide [Flame Retardant Buyers' Guide 1985].

1.7.2.3 Ammonium Polyphosphates — Water Insoluble Salts

The higher molecular weight ammonium polyphosphates are water insoluble powders and have been used in fire retardant intumescent paints. In addition, ammonium polyphosphate / ammonium bromide blends (Amgard CD, Albright & Wilson) are used to flame retard fabrics.

1.7.2.4 Melamine Phosphates

Three products are on the market [Kay, M. 1979], mono & dimelamine phosphate (Albright & Wilson), and melamine pyrophosphate (American Cyamid). They consist of finely divided solids suitable for dispersal into coatings and thermoplastics, the differences between the three are in their solubility and efficiency. The structure of monomelamine phosphate is shown in Figure 14.

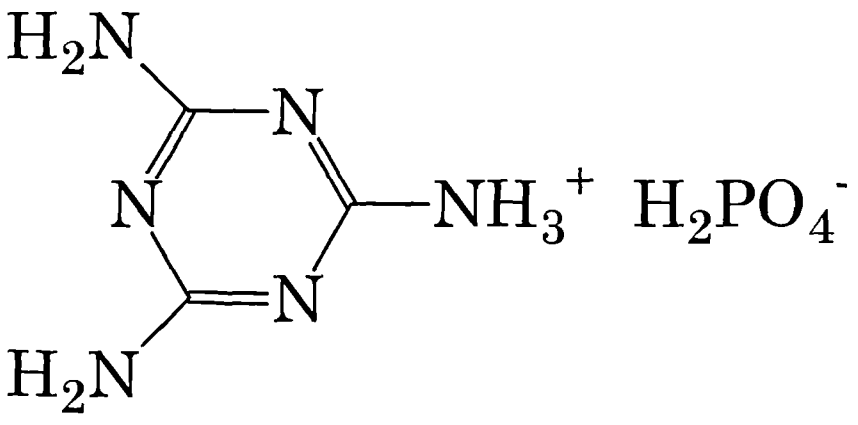


Figure 14 Monomelamine Phosphate

Dimelamine phosphate and melamine pyrophosphate have an extra one or two melamine cations and therefore one or two less hydrogens in the phosphate anion respectively.

1.7.2.5 Trialkyl Phosphates And Phosphonates

Triethyl phosphate has been in use for many years in polyester resins, it reduces their viscosity, so that they can be loaded with a high percentage of alumina trihydrate without detrimental effects. A competitive material is dimethyl methylphosphonate (DMMP, Albright & Wilson) $CH_3P(O)(OCH_3)_2$. Low volatility methylphosphonates were invented and developed by Mobil and later Albright & Wilson. They find use in rigid polyurethane foam systems and alumina trihydrate filled polyester resins.

1.7.2.6 Haloalkyl Phosphates And Phosphonates

The classic example of this type is tris(2-chloroethyl) phosphate, having an unusually wide range of flame retardant additive applications from cellulosics to polyurethane foams. However it is somewhat more volatile than other haloalkyl phosphates and in some polyurethane foam systems it's ester linkage can be reactive towards the amine catalysts used. Tris(1,3-dichloroisopropyl) phosphate (AMGARD TDCP, Albright & Wilson), Figure 15, is chemically inert due to its branched structure and is used in most flexible foam systems, as it doesnot interfere with many of the catalysts used.

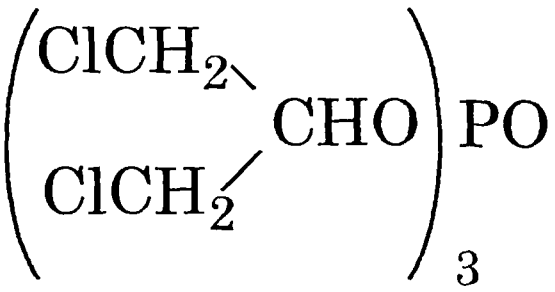


Figure 15 Tris(1,3-dichloroisopropyl) Phosphate

1.7.2.7 Chloroalkyl Diphosphates And Oligomers

Reduction in volatility of the useful chloroalkyl phosphates is required to improve their ageing performance in flexible polyurethane foams. Making use of the steric hindrance principle to gain hydrolytic stability in polyurethane foam systems is tetrakis(2-chloroethyl)dichloroneopentyl diphosphate (AMGARD V6, Albright & Wilson), see Figure 16. It is extensively used in flexible polyurethane foams and shows less scorching of the foam during production than related compounds.

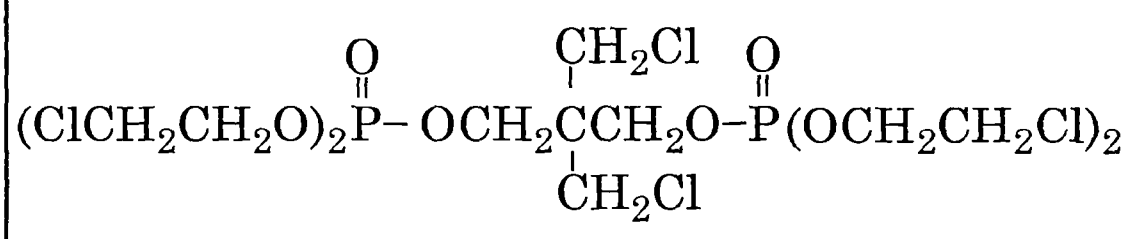


Figure 16 Tetrakis(2-chloroethyl)dichloroneopentyl Diphosphate

1.7.2.8 Triaryl Phosphates

The simplest member of this family is triphenyl phosphate which works well as a flame retardant in cellulose acetate. Isopropylphenyl diphenyl phosphate is a widely used flame retardant plasticizer for flexible vinyl and cellulosics.

1.7.2.9 Textile Finishes

By far the most widely known are a phosphonium salt–urea–ammonia cured polycondensate (Proban, Albright & Wilson) and a phosphonopropionamide (Pyrovatex, Ciba Geigy). They find extensive use in flame retarding industrial cotton and polyester/cotton blended garments.

1.7.3 Mechanism Of Action Of Phosphorus Flame Retardants

Phosphorus flame retardants have several known modes of action [Weil, E.D. 1980]. In polymers which can form a good char by dehydration, of which cellulose is the best example, phosphorus compounds appear to work by breaking down to phosphoric acid or polyphosphoric acid, which is a catalyst for dehydration [Lewin, M. 1984]. In cellulosics and rigid polyurethane foams, the char yield is increased and the flammable volatile pyrolysates are reduced.

In polymers which do not readily form chars, such as polyolefins and [poly]styrenes, phosphorus compounds tend to be less efficient unless they are formulated with well selected char forming additives e.g. ammonium

polyphosphate combined with cyclic urea formaldehyde resins in polyolefins [Bertelli, G. 1986].

Vapour phase activity can also be demonstrated. An ideal example is that triaryl phosphates which can be shown to counteract the vapour phase combustion of the poly styrene pyrolysates [Carnahan, J. 1979]. They are also believed to function as condensed phase char promoters at the same time.

The literature also supports evidence for some physical activity with some phosphorus based flame retardants [Batt, A.M. 1989]. Such modes of action are :—

i) the formation of a polyphosphoric acid surface coating.

ii) the heat sink action of a vaporising phosphorus compound.

iii) dilution of the combustible pyrolysates by a less combustible vapour.

iv) reduction of melt viscosity to favour a melt drip mode of extinguishment.

1.7.4 Toxicity And Environmental Considerations

Broadly speaking the phosphorus based flame retardants do not appear to have serious problems of acute or chronic toxicity [Muir, D.C.G. 1984]. The LD_{50} values (rat, oral) of organophosphorus flame retardants range from about 390 mg/kg to above 10,000 mg/kg, most being above 1000 mg/kg. There are a few notable exceptions, certain heterocyclic derivatives of organophosphorus esters have been shown to be delayed neurotoxins [Abou–Donia, M.B. 1990] but these are not functional flame retardants. Tris(2,3-dibromopropyl)phosphate, an excellent flame retardant was found to be mutagenic and carcinogenic in the 1970's and it was promptly withdrawn [Soderlund, E.J. 1982]. Related haloalkyl

phosphates have been extensively tested and their toxicity found to be of a much lower order of magnitude [Soderlund, E.J. 1982].

Environmental aspects of phosphorus based flame retardants have been thoroughly studied in the USA and Canada. Aquatic life is under little threat from the phosphates in certain flame retardants, as they appear to be hydrolysed and biodegraded fairly rapidly [Saeger, V.W. 1979]. The disappearance of phosphate ester from soil and water is aided by the presence of phosphate cleaving enzymes found in all living organisms. However the C–P linkage in alkyl phosphonate flame retardants is less rapidly biodegradable, but there are even a few micro-organisms present in the biosphere which will attack alkylphosphonates [Zeleznick, L.D. 1963].

1.8 Heterocyclic Derivatives Of Phosphorus

As demonstrated previously, all successful phosphorus based flame retardants have a high percentage phosphorus content (between 15% & 20%). Whilst the vast majority, almost to exclusion, are empirically analogous to straight chain (halo)alkylcarbon molecules, little or no interest has been shown in heterocyclic derivatives of phosphorus as potential flame retardants. This is surprising since a heterocyclic analogue of a straight chain (halo)alkylphosphonate ester will have an inherently higher phosphorus content than its straight chain counter part due to its ring structure.

The major objectives of the current work were to synthesise heterocyclic phosphorus compounds and to assess their flame retardant properties.

1.8.1 Phospholenes

In his patents of 1953, McCormack reported the synthesis and characterisation of seventeen products, based on a five–membered heterocycle containing one phosphorus atom, resulting from the reaction outlined in Figure 17 below [McCormack, W.B. 1953] :—

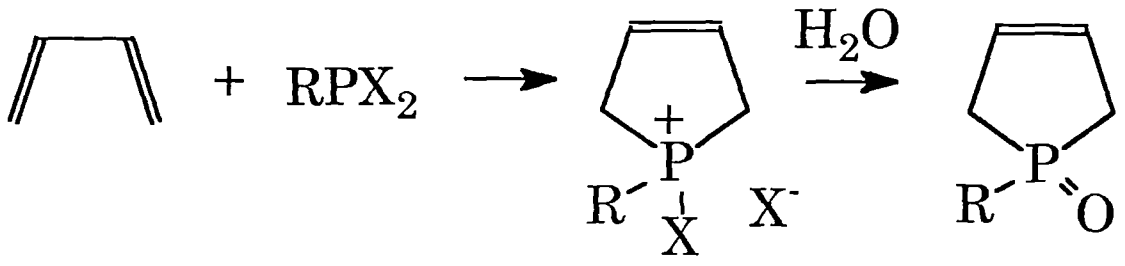


Figure 17 The McCormack Cycloaddition Reaction

The products, properly referred to as phospholene oxides, represented a new class of heterocyclic system. The intermediate cycloadducts were members of the highly reactive halophosphonium halide family. These were not isolated but were hydrolysed to the phospholene oxides which were quite stable, easily handled and purified. Following the advent of NMR spectroscopy, the cycloaddition was shown to proceed with a high product specificity with reference to the double bond migration as shown in Figure 18. The nature of the halide X determined the final position of the double bond, for X = Bromine the double bond remained in the 3–position (A), however when X = Chlorine the double bond changed to the 2–position (B).

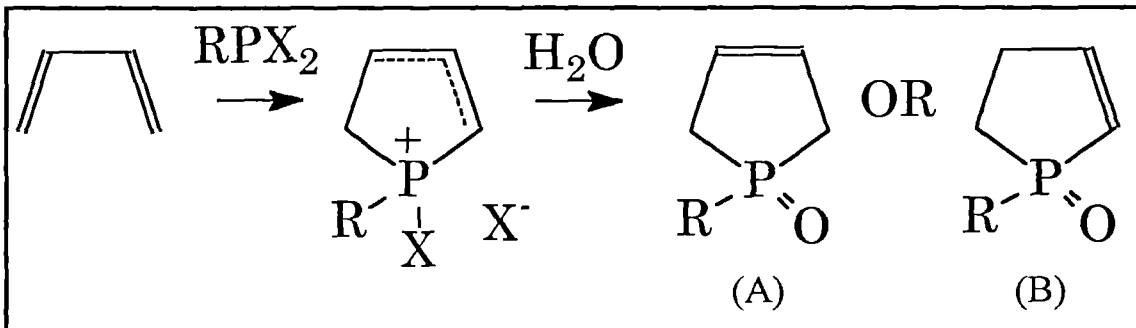


Figure 18 Bond Migration In The McCormack Cycloaddition

However, the usual procedure for conducting the cycloaddition involved leaving the diene and expensive alkylphosphonous dihalide at room temperature for prolonged periods — weeks or sometimes months. This lengthy reaction time and expensive starting material made this synthetic approach economically unviable on an industrial scale. The final product also needed to be converted into an ester to more fully imitate an alkylphosphonate ester and thus obtain the most favourable flame retardant performance based on previous knowledge and experience.

At the start of this project it was decided to take a different synthetic approach. A slight, but significant change to the starting materials and reactants mentioned above, would possibly achieve the required goal. Replacing the expensive alkylphosphonous dihalide with the more hazardous but cheaper phosphorus trihalide and then reacting the unstable intermediate with an alcohol could give the following structures, so called phospholene oxide esters shown in Figure19.

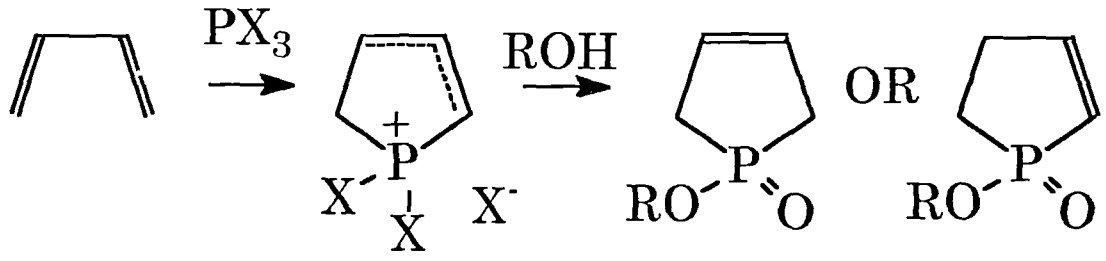


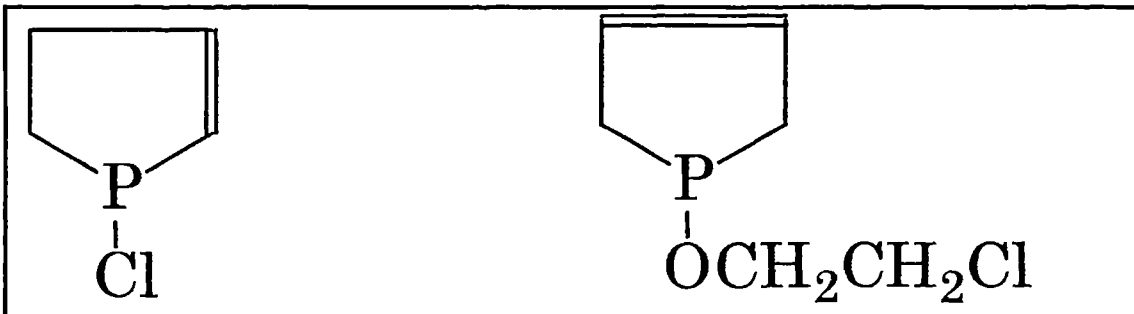
Figure 19 Proposed Initial Synthesis Scheme

If this were successful, there would then be extensive scope for modification of this base molecule through various alkyl and aryl substituents to the basic ring, with further variation from the alcohol used. A comprehensive search of the literature revealed few sources of information, none even fairly recent, on this exact topic. Of those that were available [Hasserodt, U. 1963, Hunger, K. 1964 and Quin, L.D. 1968], none had any comprehensive detail on this specific synthetic transformation, being more concerned with the work by McCormack.

2.0 The Phospholene Ring System — Previous Work

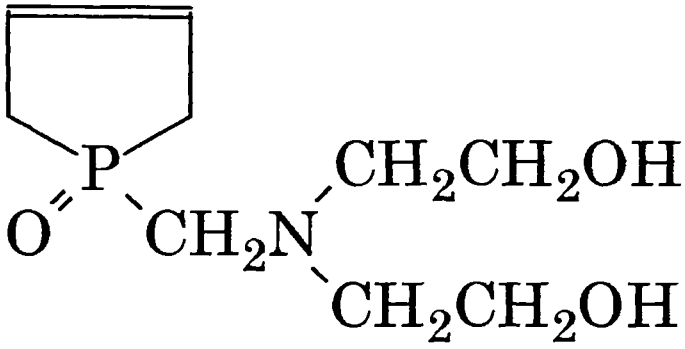
As mentioned previously, very few investigations of phospholene oxide esters have been performed [Hunger, K. 1963]. Spectroscopic analysis of a variety of phospholene oxides first identified by Hasserodt, Hunger and Korte [Hasserodt, U. 1962, Hunger, K. 1963] was carried out to identify the position of the double bond in the products from a diverse selection of reactions and also the effects of substituents on the position of the double bond in the product [Weitkamp, H. 1964]. Later work was concerned with shifting the double bond between the 3–position and the 2–position [Müller, E.W. 1964]. In 1970 investigations into the preparation of 1–halophospholenes, where the phosphorus is trivalent, were carried out. Two methods were described to derive these valuable synthetic intermediates [Myers, D.K. 1971]. A few novel heterocyclic phosphorus compounds, derived from these synthetic intermediates, were patented for use as catalysts for preparing carbodiimides from isocyanates, as surface active agents and as reactive flame retardant components of polymer systems, such as polyurethane polymers [Smith, C.P. 1973] (see Figure 20). However the commercial application of this patent has not come to fruition. Two further patents [Onder, S. 1979 and Nelb, R.G. 1988] detail respectively, the preparation of cyclic phosphorus compounds (derivatives of phospholenes, phospholanes and phosphetanes – 4 membered ring system) and their subsequent use as catalysts in the preparation of a polyamideimide semi–flexible foam with good flame retardant properties (ASTM D–2863 test : Oxygen Index 38%). Similar work on the applications of the synthetic intermediates, 1–halophospholenes, but via new approaches, was also undertaken by Russian chemists [Vizel, A.O. 1973 and Arbuzov, B.A. 1975] and

subsequently expanded upon [Berestovitkaya, U.M. 1981 and Arbuzov, B.A. 1985].



1–Chloro–2–Phospholene

1–(2–Chloroethoxy)–3–Phospholene



1–Diethanolaminomethyl–3–Phospholene Oxide

Figure 20 Novel Patented Phospholene Compounds

Studies have also been completed on the reactivity of 1–halophospholenes (tri co–ordinate compounds) with diethyl peroxide [Hammond, P.J. 1982]. The data suggested a relationship between the ^{31}P NMR chemical shift of a 1–halophospholene and its rate of reaction with diethyl peroxide, probably the electronegativity of the 1–substituent dictating the rate of reaction by stabilisation of the penta co–ordinate intermediate. Increased electronegativity of the 1–substituent causes a deshielding of the phosphorus atom and a consequent migration of the ^{31}P NMR chemical shift to a lower field. Further evidence was also

provided for the biphillic nature of the reaction between tri co–ordinated phosphorus compounds and diethyl peroxide in that the system revealed both the electrophilic and nucleophilic character of the tri co–ordinated 1–halophospholene.

The five membered ring system characterising the phospholene series has been shown to exist with the double bond in either the 2 or 3 position [Weitkamp, H. 1964]. Both structures are under ring strain and consequentially exhibit ring puckering [Harthcock, M.A. 1984]. The 2–phospholene ring system has a less puckered conformation than the 3–phospholene ring system and is therefore more stable. A lower energy

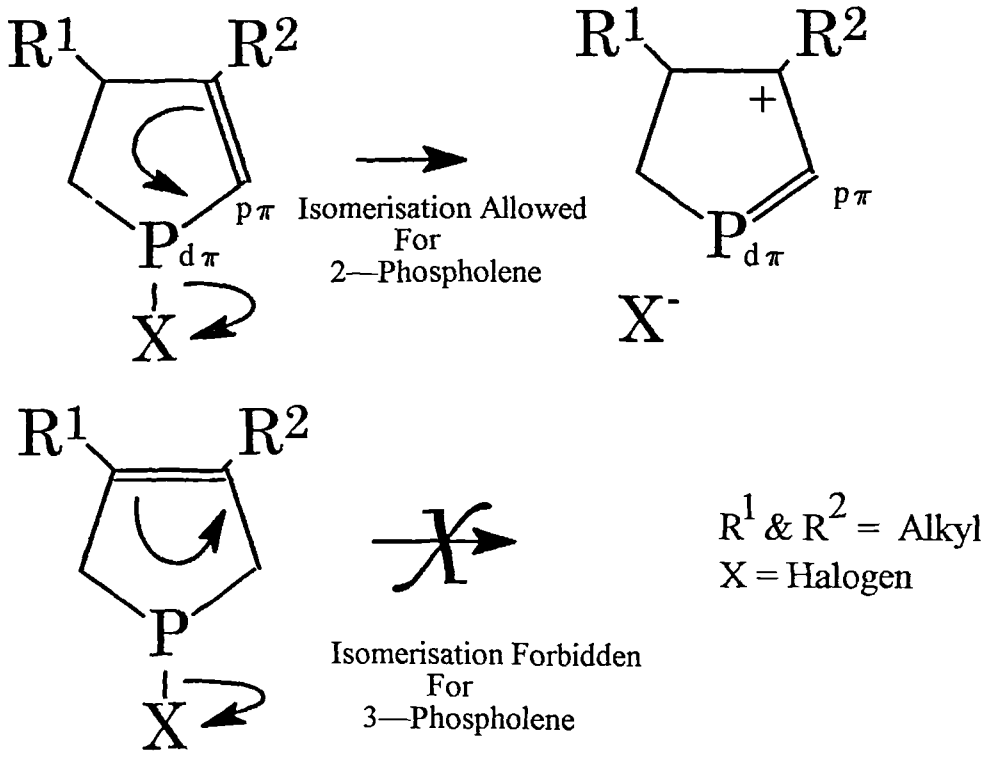


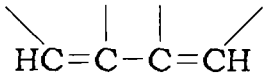
Figure 21 Isomerisation Of 2–Phospholene Ring System Via dπ—pπ Bonding Allowed In 2–Phospholene But Forbidden In 3–Phospholene

for the planar ring conformation of 2–phospholene may be an indication of some $d\pi$–$p\pi$ bonding between the phosphorus atom and the olefinic double bond [Schmude, R.W. 1987] (see Figure 21).

Recent significant advances in the development of mathematical and numerical tools enabled attempts to identify the precise classical dynamic pathway for the isomerisation and resultant conformation to be made [De Leon, N. 1989]. By using Reactive Islands (RIS or phase structures) as essential mediators of unimolecular conformational isomerisation [Marston, C.C 1989] the isomerisation was shown to be non–chaotic (regular) as opposed to chaotic (irregular) and nondissipative (phase space volume does not contract with time) as opposed to dissipative (phase space volume contracts with time but does not necessarily equilibrate). The precise time at which bond migration occurs from the 3–position to the 2–position, when reactions with halophosphonium halides are carried out is still uncertain. Bond migration can occur in either the product, during the reaction, or in the halophosphonium halide to form an ionic salt (see Figure 22).

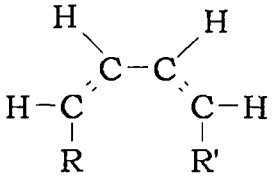
The McCormack cycloaddition (see section 1.8.1) can proceed with high product specificity. With proper choice of the alkyl or aryl phosphonous (III) dihalide reactant and conditions, it is frequently possible to obtain a pure sample of either the 3–phospholene or 2–phospholene system. The 3–phospholene system, unless stabilised by alkyl substituents on both sp^2 carbons, can also be rearranged with a base to the 2–isomer. In essence the McCormack reaction can be thought of as a special type of Diels–Alder 1,4– cycloaddition reaction, wherein the dieneophile is an aryl or alkyl phosphonous dihalide and the conjugated 1,3–diene is subject to certain limitations :—

a) The conjugated diene portion must not have more than one substituent on the terminal atoms (1– and 4– carbons).

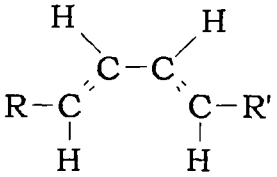


b) The diene should be free from substituent CN or CO groups.

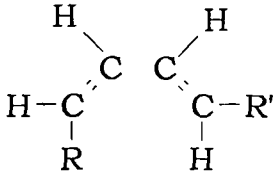
c) A 1,4– disubstituted butadiene exists in four geometrically isomeric forms, only the addition of the trans,trans form will proceed with negligible hindrance. The cis,cis form offers considerable obstruction, whilst the trans,cis and cis,trans forms offer intermediate obstruction.



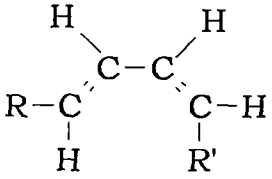
cis,cis



trans,trans



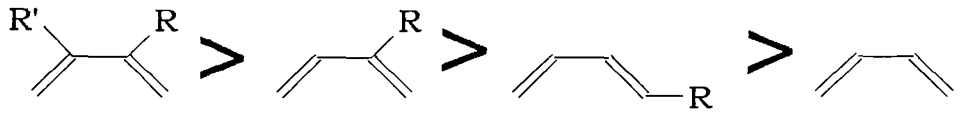
cis,trans



trans,cis

d) No carbon atom of the conjugated diene portion may be part of an aromatic ring, and no three carbon atoms may be part of the same cyclo–aliphatic ring. Compounds in which two adjacent carbon atoms of the conjugated diene portion are part of the same cyclo–aliphatic ring may be employed in the reaction.

Phosphorus trihalides can be used in place of the aryl or alkyl phosphonous dihalides [Hasserodt, U. 1963] normally used, although the reaction time is lengthened with phosphorus trichloride but shortened with phosphorus tribromide. However the trichloro intermediate gives rise to the 2–isomer in exclusion when reacted further, but conversely the tribromo intermediate gives rise to the 3–isomer in exclusion when reacted further [Hunger, K. 1964]. The trihalogenated intermediate produced is extremely reactive, hygroscopic and very sensitive to air and therefore it is unwise to store it for any length of time. The rate of a particular cycloaddition is controlled by structural features in both reactants. Phosphonous dibromides react faster than dichlorides, with alkyl derivatives faster than aryl. Phosphorus tribromide reacts faster than phosphorus trichloride which reacts slower than methyl phosphonous dihalides. For the diene, a general order of reactivity is :—



R' & R = Alkyl

Stereochemistry can have importance in the McCormack reaction. Since the phosphorus atom possesses a chiral centre, then the presence of another chiral centre in the C–2 position will result in the formation of a pair of diastereoisomers, each constituting a racemic mixture. The stereospecificity of the cycloaddition suggests it to be a concerted reaction, occurring in a disrotatory fashion [Bond, A. 1968]. This is the expected result of a 4+2 thermal electrocyclic process, cheletropic in this case. Reversibility of the McCormack process is not expected, as the ionic

product actually obtained is not the same as the initial cycloadduct (see Figure 22).

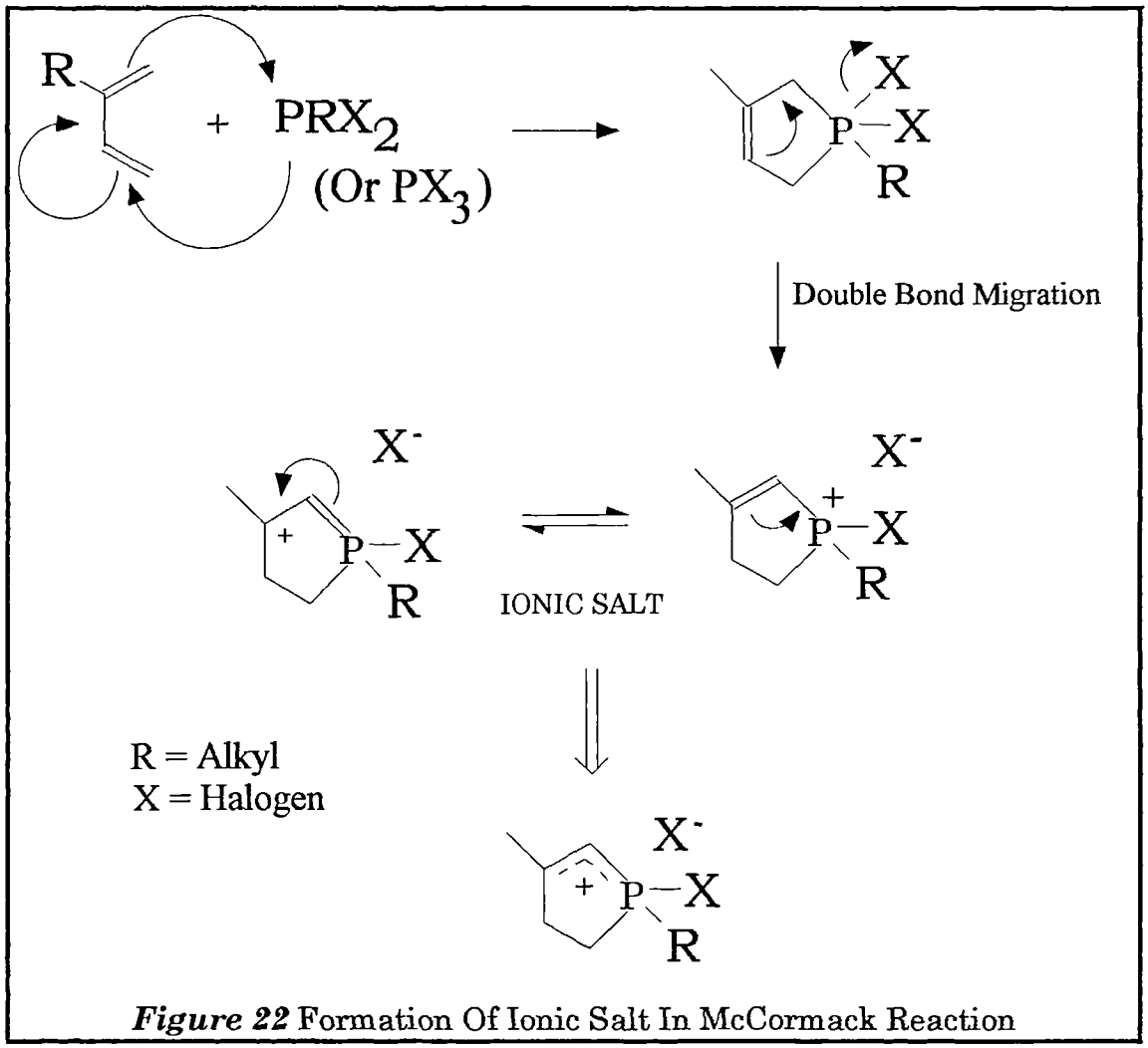


Figure 22 Formation Of Ionic Salt In McCormack Reaction

2.1 Development Of Synthesis Route To Phospholene Oxide Esters

Extensive work on studies related to the synthesis and properties of phospholene oxides formed from the reaction of methylphosphonous dichloride and phenylphosphonous dichloride with 1,3–butadiene and isoprene (2–methyl–1,3–butadiene) has been reported [Moedritzer, K. 1975, 1977, & 1978]. This information aided in the initial selection of reactants and criteria for reaction conditions for the preliminary synthesis

of the target model compound (base molecule), based on the phospholene oxide structure, for the work reported in this thesis. Choice of solvent, inclusion of adequate diene polymerisation inhibitors, control of the pH of the reaction, hazardousness and toxicity as well as physical properties of the starting materials were further points that needed to be considered in this pre–selection. Since the intermediate cycloadducts were members of the highly reactive halophosphonium halide family, the reaction would need to be carried out under inert conditions as well as in two distinct stages.

2.2 STAGE I : Synthesis Of 1,1,1–Trichloro–3–Methyl–3–Phospholene

The initial objective was to synthesise the target compound 1–methoxy–3–methyl–2–phospholene oxide, in sufficient quantity (over 500 grammes) to be able to carry out a full investigation of its flame retardant performance and effect on a polyurethane system. This was to be attempted by utilising the two stage reaction scheme outlined in Figure 23. Similar reaction schemes have been reported in the literature (see Figure 24). Firstly, the intermediate halophosphonium halide compound, 1,1,1–trichloro–3–methyl–3–phospholene, needed to be synthesised. The diene selected was isoprene (2–methyl–1,3–butadiene) as it had low cost, good reactivity and was a liquid at room temperature, therefore being easier to manage than the alternative considered, 1,3–butadiene which is a gas at room temperature. Phosphorus trichloride was chosen as the dienophile, since it was readily available from Albright & Wilson, and would facilitate formation of the phospholene oxide ester in two stages. Phosphorus tribromide, although it had better reactivity, was precluded

due to the environmental implications of the use of bromine containing compounds as flame retardants.

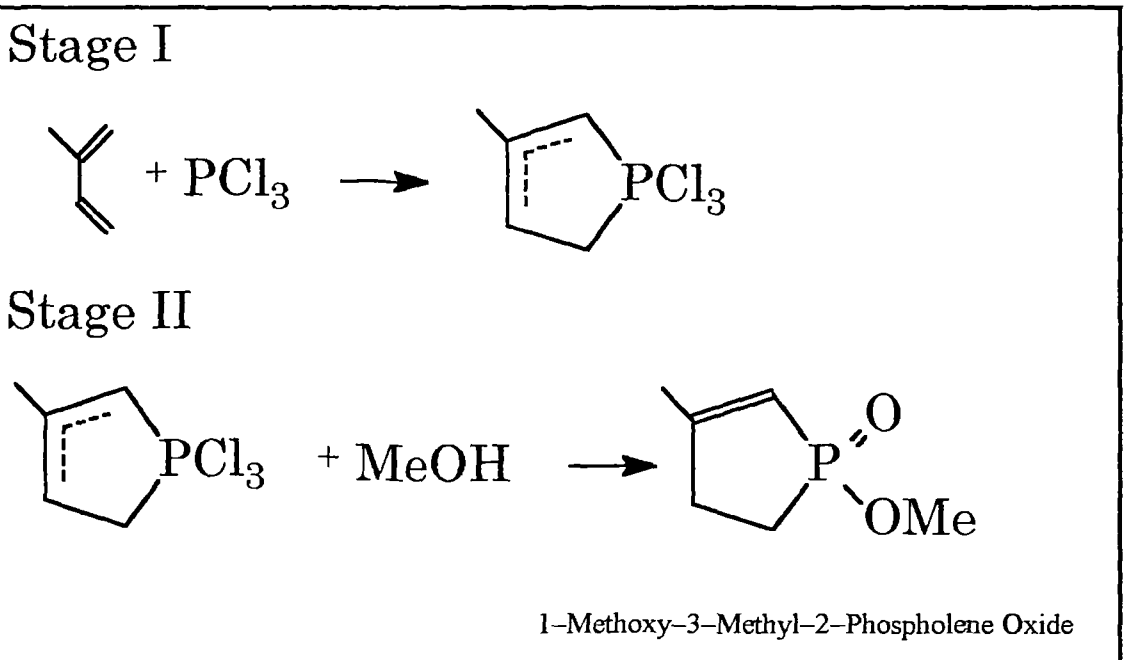


Figure 23 Proposed Synthesis Scheme For Model Target Compound 1–Methoxy–3–Methyl–2–Phospholene Oxide

All phosphorus trihalides are extremely hazardous and corrosive and extreme care was exercised at all times when using them as reactants. The nature of the product and reactants required that all of the reactions were carried out under an atmosphere of flowing dry nitrogen, the apparatus being initially purged with dry nitrogen.

The reaction scheme reported in the literature, see Figure 24, used copper stearate as a diene polymerisation inhibitor. This inhibitor was used in the first stage of the current synthesis, for exactly the same purpose. However, excess isoprene was used instead of a solvent, so that all of the hazardous phosphorus trichloride used could be reacted. It was hoped by this means to remove the inherent hazard of any excess phosphorus trichloride being present in the product. As previously described in the literature, triethylamine was used in the second stage as

a scavenger to sequester the hydrogen chloride produced and maintain basic conditions.

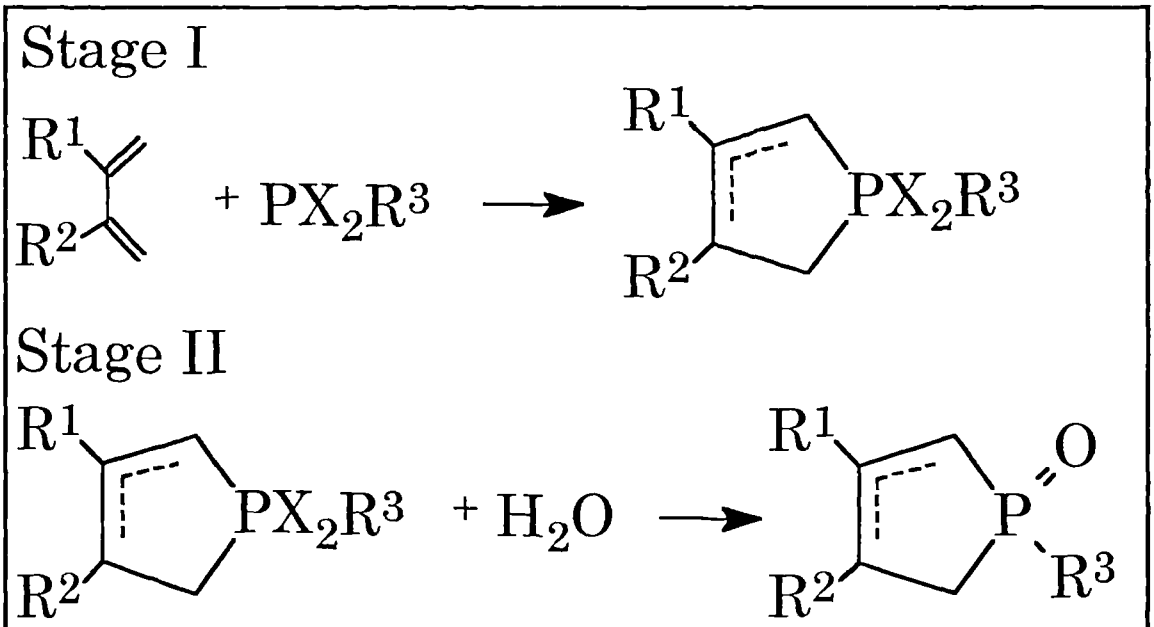


Figure 24 Reaction Scheme Reported In Literature [Hasserodt, U. 1963, Hunger, K. 1964, Quin, L.D. 1968 and Harthcock, M.A. 1984]

Previously reported syntheses of the 1,1,1–trichloro–3–methyl–3–phospholene intermediate, that is the Stage I reaction, took 20 days [Hasserodt, U. 1963, Hunger, K. 1964], or even longer [Quin, L.D. 1968, Harthcock, M.A. 1984]. In these experiments, the reactants were simply sealed in wide mouth bottle under nitrogen and left to solidify, normally taking a minimum of four weeks. This was economically and logistically unacceptable for an application with potential development to an industrial process. The ultimate goal of this research project was the realisation of a commercially viable, successful non–halogenated flame retardant for polyurethane foams. Therefore a convenient, fast synthesis

scheme needed to be identified, that produced the intermediate in high yield of at least 90%.

Iniitially, experiments were conducted using classical approaches to synthesis optimisation, that is changing one variable at a time whilst holding the other variables constant (OVAT). A series of experiments were conducted to investigate the effect of temperature, time and quantity of reactants upon the final yield of the intermediate. The quantity of reactants had little effect on the overall yield of the reaction, the only implications of using larger quantities of reactants were the size of apparatus required, the increase in the hazardousness of the reaction and the generation of large quantities of hydrogen chloride as a by–product which needed to be removed via alkaline scrubbers. The effect of time and temperature on the reaction are detailed in Table 2.1.

The results in Table 2.1 show that the yield increases within the temperature range 25°C – 50°C but decreases above 50°C. This is because at high temperatures the diene, in this case isoprene, polymerised despite the presence of the polymerisation inhibitor copper stearate and thus the yield was dramatically reduced. Also isoprene has a low boiling point (34°C) and an extremely efficient condenser was required to prevent further loss through vaporisation. At lower temperatures the reaction time is lengthened considerably, as had been found to be the case when using butadiene instead of isoprene [Hasserodt, U. 1963].

A convenient reaction scheme was identified, giving good yields in excess of 80%, a substantial improvement from the literature. The temperature of the reaction proved to be of critical importance, it being vital to maintain a consistent temperature of 50°C throughout the entire reaction time. Any decrease or increase of the temperature has an adverse effect upon the final yield of product.

Table 2.1 Reaction Conditions And Yields For Stage One

Reaction Time And Temperature	Yield	References
10 days at 25°C	61%	Hasserodt, U. 1963
28 days at 25°C	85%	Quin, L.D. 1968
20 days at 20°C	90%	Hasserodt, U. 1963
24 hrs at 60°C	25%	This Work
20 hrs at 60°C	33%	This work
10 hrs at 50°C	30%	This Work
3 hrs at 50°C	24%	This Work
20 hrs at 35°C	50%	This Work
20 hrs at 50°C	**80%**	**This Work**

2.2.1 Method Of Synthesis Of 1,1,1–Trichloro–3–Methyl –3–Phospholene : STAGE I

The experimental procedure for Stage I preparation of this compound (see Figure 25) is outlined below.

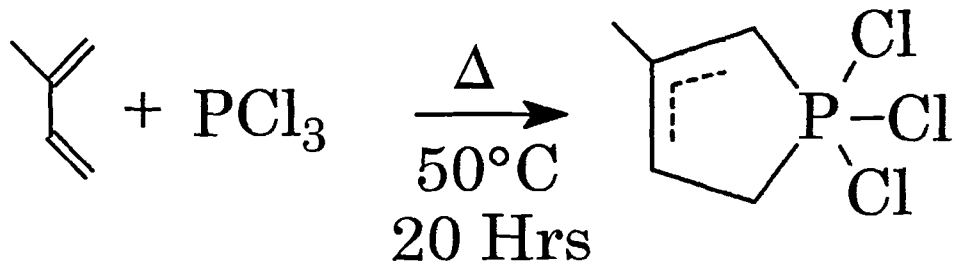


Figure 25 Stage I Synthesis Of 1,1,1–Trichloro–3–Methyl –3–Phospholene.

Chemicals Used :—

Copper Stearate synthesised from stearic acid and copper nitrate solution.
Phosphorus Trichloride obtained from Albright and Wilson (98%).
Isoprene obtained from Janssen Chemica (99+% stabilised with 100 ppm 4–tert–butylcatechol).

Using apparatus set up as illustrated in Figure 26, three moles (261 mls) of phosphorus trichloride were slowly added dropwise, via a pressure equalisation dropping funnel, to three moles (300 mls) of 2–methyl–1,3–butadiene (isoprene) and 1g of copper stearate polymerisation inhibitor under an initially vigorously flowing dry nitrogen atmosphere (30 mls min^{-1}), such that the reactants are agitated in addition to being stirred by means of a 40 mm oval Teflon coated stirrer bar (120 revs min^{-1}). After the addition, the pressure equalisation dropping funnel is replaced with a thermometer and the solution is heated to 50°C, with a heater/stirrer mantle, and held at that temperature for 20 hours under a gently flowing atmosphere of dry nitrogen (4 mls min^{-1}), such that the loss of volatiles is minimised. The solution turned white and then pale yellow in colour and an orange/red precipitate started to form after approximately one hour. After two hours the precipitate was red/brown in colour and started to thicken and rotation of the Teflon coated stirrer bar was impaired and eventually stopped. After 20 hours the whole reaction mixture had solidified into a red/brown solid, the product 1,1,1–trichloro–3–methyl–3–phospholene, in an 80% — 90% yield (500 g — 550 g). The solid product was removed whilst it was still warm, as this facilitated its easier removal, and then broken up and washed with petroleum ether (40°C–60°C fraction, 3 x 500 mls). I.R analysis identified the product as 1,1,1–trichloro–3–methyl–3–phospholene molecular weight

205.5, other analysis techniques were not employed due to the hygroscopic and hazardous nature of the product and the fact that it is unstable in air.

The apparatus set up for the experiment is illustrated in Figure 26. The use of a large double helix condenser is essential to minimise the loss of isoprene through vaporisation. Hydrogen chloride gas and any phosphorus based acid or chloride vapour, formed via side reactions with any impurities, were removed from the system by potassium hydroxide scrubbers. This minimised the attack on the PVC tubing used (silicone tubing was found to be unsuitable as it is depolymerised by the vapours), which had to be replaced after 2–3 runs in any case as it began to show signs of perishing. The entire system is vulnerable to phosphorus trichloride, since this chemical even attacks glass. The round bottom flask used should be replaced after 3–4 months of experimental use as it becomes dangerously susceptible to fracture at its base. The phosphorus trichloride also needs to be distilled periodically to overcome decomposition into hydrogen chloride and phosphorus acid. Phosphorus acid (known as "Yellow Peril") forms at all the joints of the glass apparatus used in the experiment, even though Teflon seals were used. It is highly unstable in air and should not be allowed to build up. Phosphorus trichloride can also react with the silicates in glass and occasionally form small white deposits inside the glass apparatus, these silicate deposits can be removed by immersion of the contaminated apparatus in a potassium hydroxide solution bath. Between experiments, all the apparatus was thoroughly cleaned and dried to avoid any hazards that might occur in subsequent experiments, e.g. presence of moisture.

Storage of 1,1,1–trichloro–3–methyl–3–phospholene for any length of time is inadvisable since the compound will react with any moisture to form a mixture of products (see Figure 27) and will also generate hydrogen chloride on standing for short periods of time.

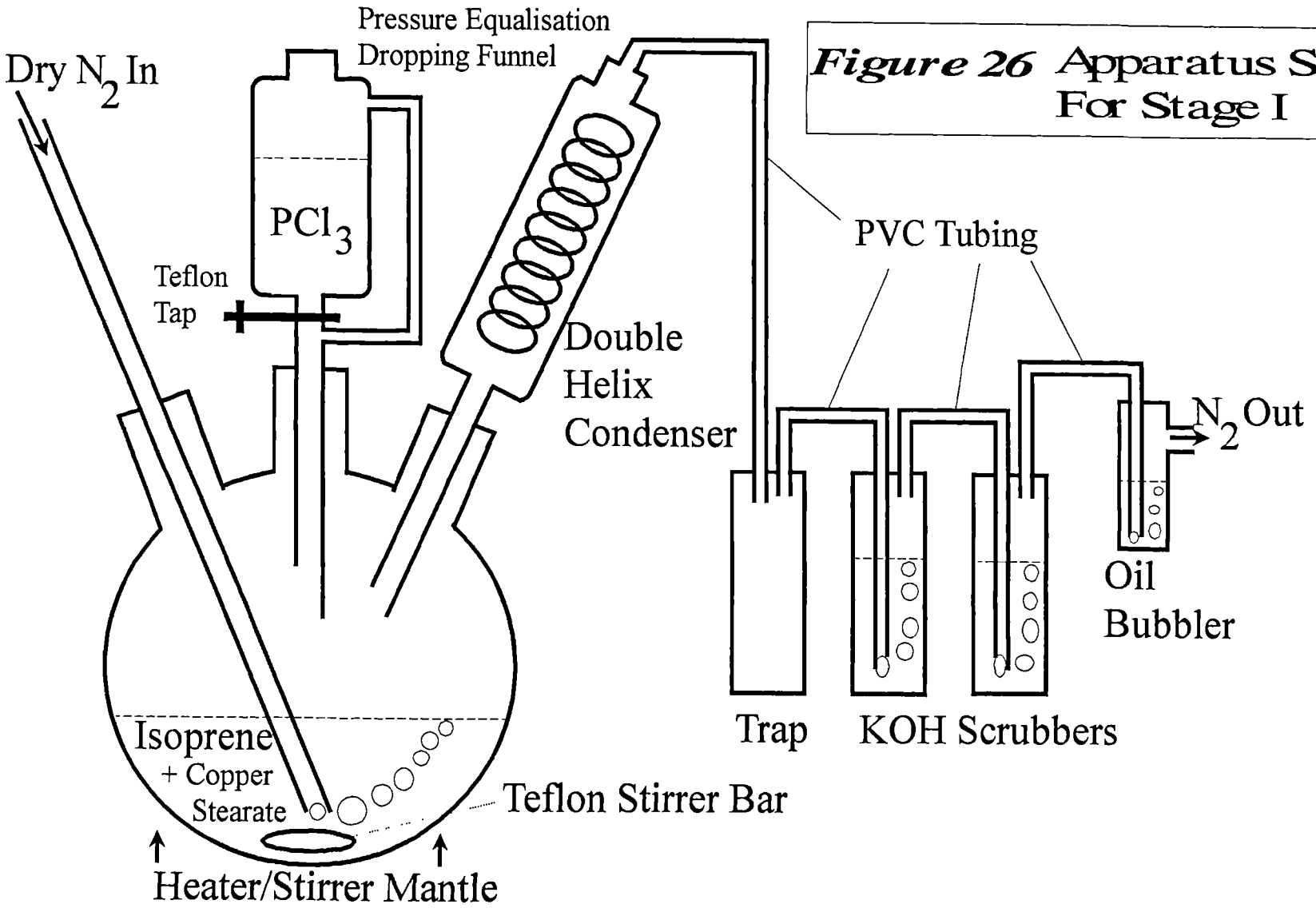


Figure 26 Apparatus Set Up For Stage I

Having identified a synthesis route which attained a greater than 80% yield of the intermediate in the comparatively short time of twenty hours, the second and final stage of the synthesis route could be developed. It was also imperative that this step in the synthesis was

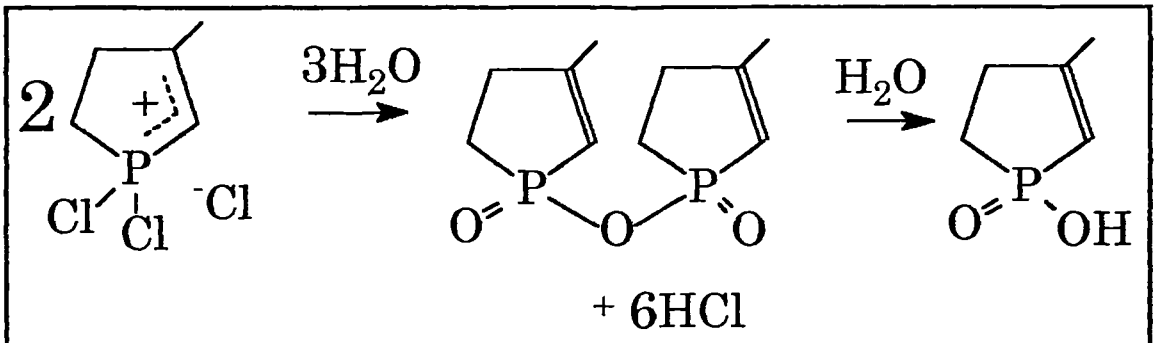


Figure 27 1,1,1–Trichloro–3–Methyl–3–Phospholene Reactions With Moisture (Storage Difficulties)

optimised to the same levels or greater, as in Stage I, so that the process had the potential to be economically viable on an industrial scale. If only the first stage had a yield in excess of 80%, then a yield of less than 80% yield for the second stage would imply an overall yield of less than 64% for the entire synthesis. This would make the process too costly and wasteful because the intermediate 1,1,1–trichloro–3–methyl–3–phospholene would have reacted and would not be available to be re–cycled.

2.3 STAGE II : Synthesis Of 1–Methoxy–3–Methyl–2–Phospholene Oxide

The minority of literature available on this synthesis step was extremely tentative about any experimental procedure, reporting yields of between 10—20% [Hasserodt, U. 1963, Quin, L.D. 1968, Cittern, P. 1987]. A variety of different conditions were used within a broad experimental

approach of slowly adding a mixture of distilled triethylamine and distilled methanol to a solution of 1,1,1–trichloro–3–methyl–3–phospholene under an atmosphere of flowing nitrogen, with subsequent neutralisation by hydrochloric acid, and when necessary saturated sodium hydrogen carbonate solution. The aqueous layer was subsequently extracted with methylene chloride to give the required product. The organic layers were then recombined and the solvent removed, leaving the product in poor yield.

This synthetic route was investigated to ascertain the yield of product. Using classical approaches to optimise the second stage of the synthesis (OVAT), a series of experiments was conducted to investigate the effect of temperature and time upon the final yield of the product. The yields of 1–methoxy–3–methyl–2–phospholene oxide, were poor as shown in Table 2.2.

Table 2.2 Reaction Conditions And Yields For Stage II

Reaction Time And Temperature	Yield	References
2 Hrs at -10°C	18.5%	Quin, L.D.1968
2 Hrs at -20°C	5%	Cittern, P. 1987
1 Hr at +20°C	5—10%	Cittern, P. 1987
4 Hrs at -10°C	20%	This Work
1 Hr at 0°C	18%	This Work
1 Hr at +10°C	5%	This Work
1 Hr at -30°C	6%	This Work
4 Hrs at +10°C	3%	This Work
1 Hr at -15°C	22%	This Work

The best reaction conditions identified, gave poor yields of about 22%, a slight improvement over the literature. Altering the temperature and the time of the reaction independently proved to be of little significance in increasing the yield. Factors that could contribute to these observed poor yields, were the exothermicity of the reaction causing the temperature to rise during the addition of the triethylamine/methanol mixture. A reduction in the quantity of 1,1,1–trichloro–3–methyl–3–phospholene used, or greater dilution, might overcome this temperature rise. The effluent precipitate of triethylammonium chloride generated in vast amounts hinders the reaction, having a "clogging" effect. Conducting the reaction in acidic conditions, i.e. without triethylamine, would overcome this precipitate problem.

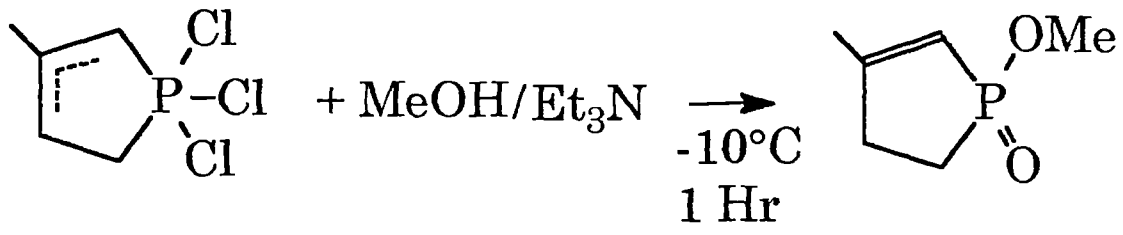


Figure 28 First Preparation of 1–Methoxy–3–Methyl–2–Phospholene Oxide :— Stage II Synthesis

2.3.1 Method Of Synthesis Of 1–Methoxy–3–Methyl –2–Phospholene Oxide : STAGE II

The experimental procedure for Stage II (see Figure 28) giving the as yet best obtainable yield, is outlined overleaf.

Chemicals Used :—

Methylene Chloride (99.6% reagent grade) from either BDH or Fisons.

1,1,1–Trichloro–3–Methyl–3–Phospholene synthesised as noted earlier.

Triethylamine (99%) from Aldrich, distilled.

Methanol (99.9% reagent grade) from either BDH or Fisons, distilled.

Using the apparatus set up illustrated in Figure 29, to 200 mls of methylene chloride was added 100g (0.5 mole) of 1,1,1–trichloro–3–methyl–3–phospholene and the solution was stirred for one hour and cooled to -20°C. A solution of anhydrous distilled methanol 61 mls (1.5 moles) in distilled triethylamine 208 mls (1.5 moles) was then slowly added over one hour, keeping the temperature at -10°C, by means of a refrigerated cooling coil and thermostatically controlled bath with circulator, which contained a mixture of ethylene glycol and water. Due to the exothermicity of the reaction it was impossible to accurately maintain a constant temperature, rather a temperature range of -5°C to -15°C was more feasible. Potassium hydroxide scrubbers were used to remove any surplus hydrogen chloride gas, evolved during the reaction, that was not "mopped up" by the triethylamine. After the end of the addition 300 mls of water (+ 10 mls 6MHCl) was added, to neutralise the solution creating two layers. If necessary saturated sodium hydrogen carbonate solution can be used to obtain neutral conditions. The methylene chloride (organic) layer was separated and the aqueous layer extracted with methylene chloride (3 x 200 mls). The organic layers were recombined and the solvent removed on a rotary evaporator leaving a dark orange/red oil molecular weight 146, b.pt. 70°C (0.4 mm) in 22% yield. Full spectroscopic analysis (GC/MS, CI MS, EI MS, ^{31}PNMR, ^{1}HNMR, ^{13}CNMR and IR) confirmed the product as 1–methoxy–3–methyl–2–phospholene oxide.

Attempts to optimise the yield for Stage II of the reaction by classic traditional methods i.e. changing one variable at a time, gave no significant improvement in the yield. The yield must therefore depend on a number of different variables, and these variables are almost surely correlated rather than independent. Therefore procedures that make it possible to consider the joint influences of all variables simultaneously was required in order to optimise the reaction. Such multivariate techniques are available [Schwindt, M.A. 1990] and are in common use in industrial situations, but are rarely applied to synthetic research problems. These kinds of techniques are encapsulated in the term Chemometrics.

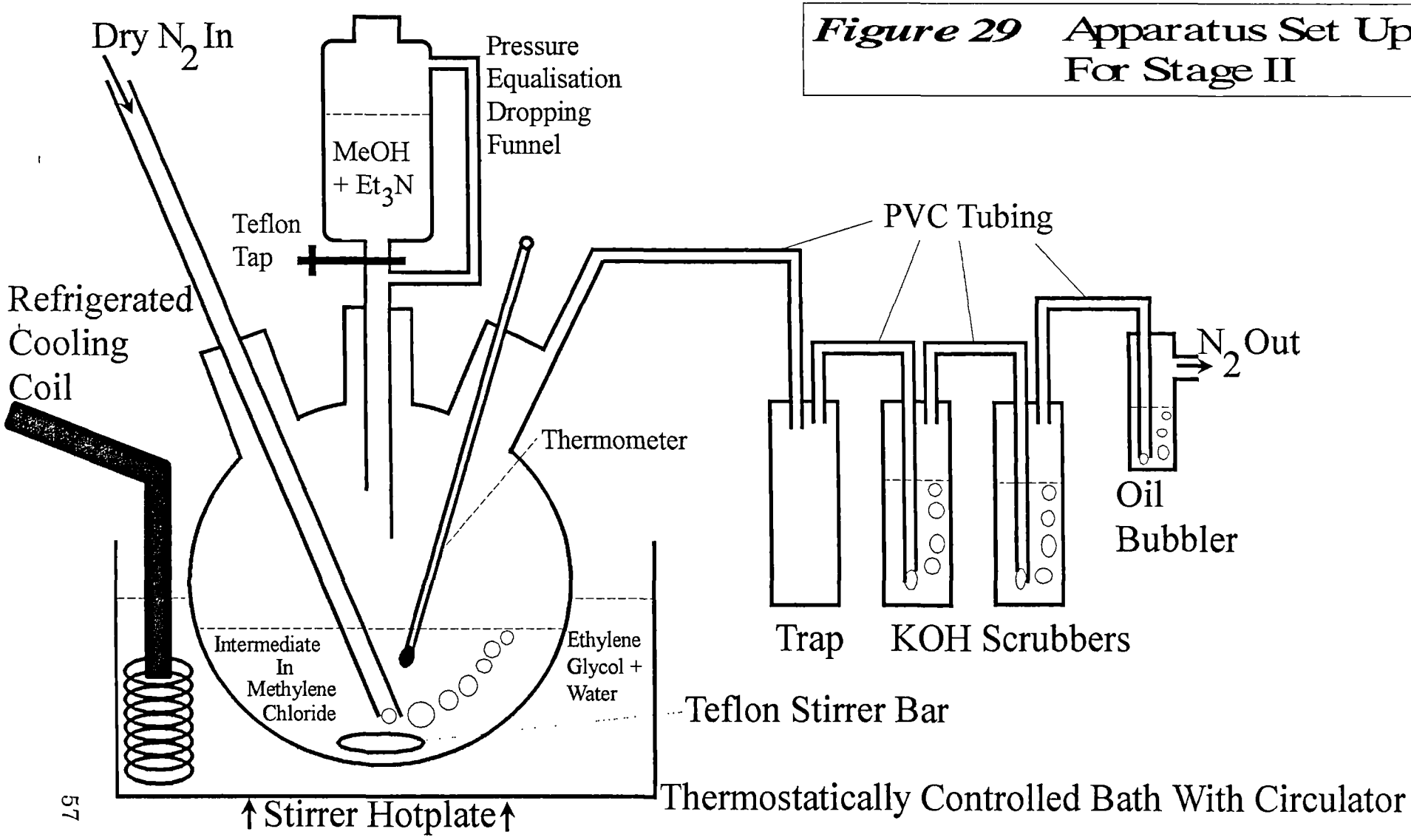


Figure 29 Apparatus Set Up For Stage II

3.0 Chemometrics — Experimental And Statistical Design

Most chemists are familiar with, if a little intimidated by, statistical analysis methods. Far fewer have even heard of experimental design methods, let alone are familiar with them. However, as was pointed out by the eminent statistician George Box — "Of these two methods, design is by far the most important. If the experimental design is poorly chosen, not much relevant information can be extracted from the data; however if the design is wisely chosen, a great deal of information is readily extractable" [Box, G.E.P. 1978].

"Science is as subjective and psychologically conditioned as any other human behaviour." Albert Einstein 1934.

Every scientific observation or measurement is a comparison, and it is up to the scientist to judge what it means and form a conclusion as to what to do with the result. The scientist has to do this as objectively as possible, trying to decide what is truth and not what he (or the boss) might want to call truth. The scientist must therefore reduce the errors and uncertainties as much as possible, the residuum left over can then usually be called scientific truth.

Chemometrics is the chemical discipline that uses mathematical and statistical methods

i) to design or select optimal measurement procedures and experiments.

ii) to provide maximum interpretation of chemical data.

Its history and origins started with W.R. MacDonnell who in 1902, used factor analysis in criminal anthropology to try and differentiate the criminals from a group composed of 1000 criminals and 1000 Cambridge students. He succeeded, but found that the differentiation was due to

background and upbringing, rather than any anthropological trait. Many papers on factor analysis, the application of multivariate data analysis methods to extract useful and often hidden data, followed in the next seventy years, until in 1971 S. Wold coined the phrase Chemometrics in a paper published in 1971. Then in 1974, S. Wold and B.R. Kowalski founded the International Chemometrics Society, with the axiom that Chemometrics is a science enabling efficient and economic data acquisition on system variables and variable interactions, which then represents this information in a simplified manner.

3.0.1 Approaches To Research Design And Optimisation

In essence, there are two accepted possibilities :–

- Change One Variable At a Time, what is known as the classical method, often referred to as OVAT optimisation.

- Change one or more than one variable from one experiment (test) to the next, this is known as the statistical design approach, often referred to as multivariate optimisation.

The first method is necessary if one seeks to understand the fundamental relationship between cause and effect, and is the basis on which theories of equilibria and kinetics have been founded. It usually involves very detailed studies based on small quantities of carefully selected materials in the laboratory.

The second method is the empirical one of directly measuring the effects of various changes in conditions without necessarily concerning oneself with the precise and intricate nature of the mechanisms producing

the observed effects. However, it is possible to at least speculate on reaction mechanisms on the basis of the results obtained. The method is therefore well adapted to optimisation and other process definition studies, although the scientist will not make changes without forethought. It is certainly important to interpret the results in scientific terms, for statistical analysis implies that there is some slight possibility that the results are in fact due to statistical error variance and not due to the chemical factors the analysis has identified. This is, however, only the case when chemical factors generating very small effects are under close scrutiny and investigation. Confusion of correlation with causation can also occur with statistical methods, that is correlation between two variables X and Y often occurs because they are both associated with a third unknown factor Z e.g. a trace impurity in one reagent. By using sound principles of experimental design and randomisation, data can be generated that provides a more sound method for deducing causality. A third source of error can be due to complexity of effects, experimental design enables the generation of data so that not only linear and additive effects, but also effects of the interactive and nonlinear kind may be estimated, with the smallest possible transmission of experimental error.

The immense power of the statistical design approach is that it can generate results much more efficiently than by the classical method, and in addition, generates further important information on the interactions between variables, which the classical approach can never provide due to the failure of the design to incorporate multivariate change. This is best illustrated by reference to Figure 30. Here the OVAT technique has been used in an attempt to optimise the yield of a reaction governed by two variables A and B. The yield of the reaction for a range of values of both A and B are depicted by the yield contours of the reaction, each contour line

representing a particular yield, analogous to the contours on a map representing the height at that point.

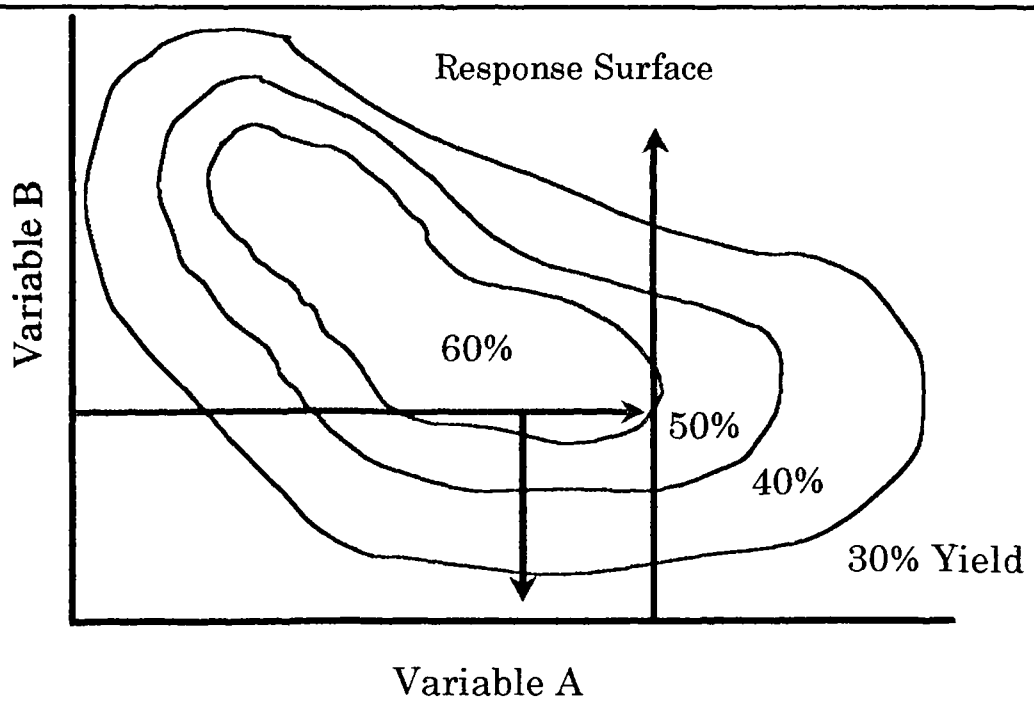


Figure 30 Depiction Of OVAT Optimisation Technique Using Yield Contours Of A Reaction

Using OVAT techniques, variable A is fixed, variable B is investigated and the yields recorded (Blue line). Variable A is then investigated, with variable B fixed and the yields recorded (Green line). As indicated in Figure 30, in neither instance do the experiments coincide with the maximum yield (Black line).

The maximum yield "can" be obtained using OVAT techniques if the initial critical choice of the pre–specified level of variable A is serendipitous i.e. A or B is fixed at a value which coincides with that of the summit of the response surface. However, it is rare to find that only two variables govern the yield of a reaction and that the variables are not interactive.

3.0.2 The Advantages Of Statistically Designed Experiments

The term optimisation is used in many contexts of organic synthesis, usually signifying the adjustment through experimentation of reaction variables (temperature, concentration, pH, time etc.), to obtain maximum yield of product, or minimum yield of impurities. The term can also be used as a synonym for 'systematic search for improvement' in a desired response or result.

When reaction mechanistic details are known, it is sometimes possible to deduce, by theoretical scientific reasoning, how to improve the response (result). With new reactions, however, mechanisms are still unknown or at best only postulated theories, and it is unlikely that accurate knowledge of the reaction will be revealed before the usefulness of the reaction has been demonstrated. This, consequently implies that a method of optimisation must precede a mechanistic understanding, and must accordingly be accomplished through experimental, investigation.

Chemical phenomena rarely depend upon single factors, many variables will normally exert an influence on the result of any chemical manipulation. To further complicate the situation, it is often the case that several of these variables will also exert interactive effects on other variables, i.e. in addition to a direct influence, some variables will also modify the influence of other variables on the overall chemical phenomena observed. This is the reason why OVAT optimisation often fails where multivariate methods, which make it possible to consider the joint influences of all variables simultaneously, succeed [Duckworth, W.E. 1968].

A synthetic reaction can be thought of as an 'event' or 'action' which can be applied in a variety of ways to a finite number of substrates and in this respect, the event may have a broad scope, see Figure 31.

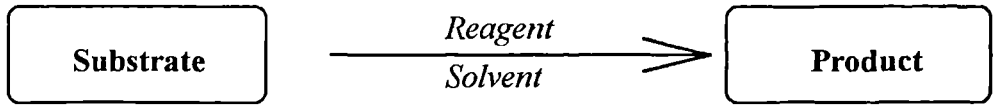


Figure 31 A Synthetic Reaction – 'Event'

Both the reagent and solvent may be modified, constituting discrete changes in the reaction system, the amalgamation of all such discrete variations is termed the reaction space. In addition, the actual experimental conditions can be varied in an infinite number of ways, but being under control of the investigator they can be adjusted to predetermined levels within the experiment. Such variations are said to occur within the experimental space, see Figure 32.

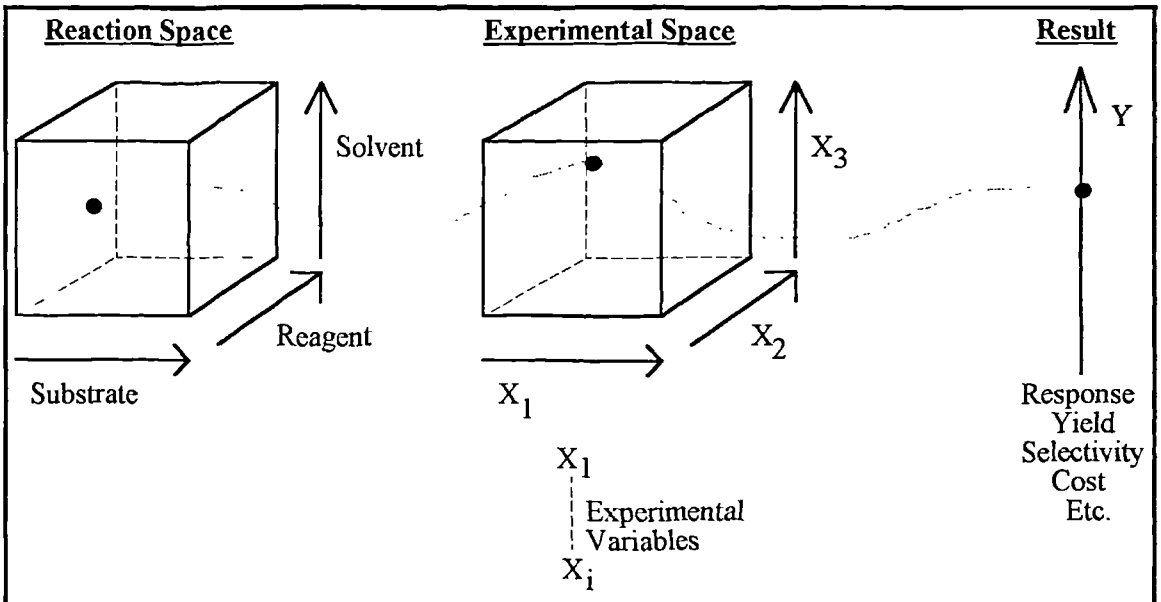


Figure 32 Reaction Space And Experimental Space

This means that any optimisation will need to explore both the reaction and experimental spaces, to find the best reaction system (reagent & solvent) to achieve the desired transformation of a given substrate and the determination of the optimum configuration of the experimental variables for the system. The best reaction system can

normally be identified by application of currently known scientific and chemical principles of transformation to the specific type of substrate transformation required. Several common problems in organic synthesis are located in the reaction space, as a desired transformation can often be achieved by several reagents in any number of solvents. The common approach in these examples is to use OVAT methods of investigation, although no account of interaction effect between variables will be acknowledged. The difficulty in applying multivariate methods to the reaction space is that firstly it is necessary to quantify the axes and secondly a discrete variation in the substrate or reagent will change a number of intrinsic properties of the substrate or reagent, e.g. a change of substituent in the substrate will alter the steric environment, electron distribution, hydrogen bond ability etc. of the substrate and will be of primary importance in determining the substrate's chemical behaviour. An approach to the problem is to use principal properties to describe any substrate and the systematic variations in the reaction space [Carlson, R. 1987].

The obstacle in experimental space is that the variations depicted in Figure 32 are not independent and the only way to detect such important variable interactions is to carry out experiments in which all intervening important variables are allowed to vary simultaneously, via the use of statistically designed multivariate investigative methods.

3.0.3 Investigating The Experimental Space

Assuming that the reaction space is acceptable, i.e. the substrate can be transformed albeit inefficiently by the reaction system selected (but there appears scope for further development), the experimental space must then be investigated.

In any synthesis there are a large number of factors that can be varied, in most cases only a few of them will have any real influence. If the investigator is unable to identify these few influential factors through knowledge and understanding of the synthesis, a preliminary screening of the variables will be necessary. Simplex EVolutionary OPerationS (EVOPS) [Box, G.E.P. 1969] can be used to examine n variables at three levels with (n+1) experiments irrespective of the size of n. However, simplex EVOPS can be expected to work well when empirical feedback is the only consideration.

3.0.4 Investigating The Effects Of Three Variables

The most common situation encountered in synthesis optimisation is the investigation of three variables A, B and C on reaction yield — the obvious variables likely to be most significant are temperature, time and concentration, although there could be others, e.g. presence of catalyst, pH, origin of raw material, flow rate etc. The statistical investigation of three variables is conducted by operating the reaction at two levels of each variable (commonly called high and low).

If one were to use the classical approach, it would require a minimum of 24 experiments to investigate the three variables at the two chosen levels i.e. (N^{o}. of levels) x (N^{o}. of variables) x (N^{o}. of combinations of two variables {n-1} at high and low levels) = 2 x 3 x 4 = 24 experiments. That is, to investigate variable A at both levels requires the following initial experiments,

(1)Low A at Low B and Low C,

(2)High A at Low B and Low C,

Thus experiments investigating the effect of changing variable A with B and C held at their low levels could be performed to give an estimate of the effect of variable A on the reaction (similar to the OVAT approach illustrated in Figure 30), but only at **low** B and **low** C, i.e. no information would be available on the effect of changing variable A at any other levels of variables B and C. To investigate the effect of changing variable A at these other levels of variables B and C would require a further six experiments. Then after eight experiments, the complete effect of changing variable A on the reaction would be known. One could then hold the value of variable A at the supposed optimum, whilst the effect of variable B was investigated. This would require a further four experiments to investigate the effect of changing variable B on the reaction. Finally to investigate the effect of changing variable C on the reaction would require two further experiments, with the variables A and B held at their optimum levels. However the effect of changing variable B on the reaction was ascertained from a specific value of variable A, i.e. it is not the same as the complete effect of changing variable B on the reaction. This is also true for the effect of changing variable C on the reaction, as it was ascertained from specific values of variables A and B. To ascertain the complete effect of either variable B or C would require a set of eight experiments, analogous to the set of experiments used to investigate the complete effect of variable A on the reaction. It would therefore require a minimum of twenty four experiments to fully ascertain the complete effects of each of the three variables on the reaction.

The multivariate experimental and statistical design approach is a much more direct and efficient method for optimisation. With this method, using a factorial design approach, there are **eight** possible **combinations** of the **three variables** at **two levels**, see Table 3.1.

These eight individual experiments, called treatment combinations (TC'S) by statisticians, are the total number of possible combinations of three variables each at two levels ($8 = 2^3$), and it is called a 2^3 full factorial experiment (similarly an investigation of five variables at two levels leads to a 2^5 experiment with 32 treatment combinations).

The statistician's symbols for the TC'S are shown in the last column in Table 3.1, arising from the following convention.

> *The presence of a variable at its high level is signified by the inclusion of the corresponding lower case letter assigned to that variable in the TC. The presence of a variable at its lower level is indicated by an absence of the lower case letter assigned to that variable in the TC, e.g. ac infers high A, low B and high C, c infers low A, low B and high C, (1) infers low A, low B and low C.*

Table 3.1 A 2^3 Full Factorial Experiment

Experiment	Variable A	Variable B	Variable C	Treatment Combination
1	low	low	low	(1)
2	high	low	low	a
3	low	high	low	b
4	high	high	low	ab
5	low	low	high	c
6	high	low	high	ac
7	low	high	high	bc
8	high	high	high	abc

The experiments (TC'S) must be performed in a random order, this is essential, as it is important, for example, not to investigate all the high temperature reactions of a set first and all the lower ones later. If this is done, a change caused by, for example, deterioration of reagent in storage may be ascribed to the effect of temperature. However the raw data, i.e. responses, must be analysed in a pre–specified order (that shown in Table 3.2).

Table 3.2 Yates' Table Of Analysis Of A 2^3 Full Factorial Design (3 variables)

	Columns Of Analysis		
Response	1	2	3
(1)	(1) + a	(1) + a + b + ab	(1) + a + b + ab + c + ac + bc + abc = Sum of Responses
a	b + ab	c + ac + bc + abc	a - (1) + ab - b + ac - c + abc - bc = $4Eff_A$
b	c + ac	a - (1) + ab - b	b + ab - (1) - a + bc + abc - c - ac = $4Eff_B$
ab	bc + abc	ac - c + abc - bc	ab - b - a + (1) + abc - bc - ac + c = $4Eff_{AB}$
c	a - (1)	b + ab - (1) - a	c + ac + bc + abc - (1) - a - b - ab = $4Eff_C$
ac	ab - b	bc + abc - c - ac	ac - c + abc - bc - a + (1) - ab + b = $4Eff_{AC}$
bc	ac - c	ab - b - a + (1)	bc + abc - c - ac - b - ab + (1) + a = $4Eff_{BC}$
abc	abc - bc	abc - bc - ac + c	abc - bc - ac + c - ab + b + a - (1) = $4Eff_{ABC}$

A rapid and simple method of calculating the effects in factorial design is the Yates' algorithm [Box, G.E.P. 1978], which consists of adding and subtracting the responses in successive pairs for as many columns of analysis as there are variables.

Table 3.2 illustrates these operations for the case of a 2^3 full factorial design using the TC symbols as results. The first four entries in the first column of analysis are obtained by adding the successive pairs of responses together and the lower four entries by subtracting the top number of each pair from the lower number. The second column of analysis is obtained by repeating this procedure on the results in the first column, the third column of analysis is derived in a similar manner from the second column. The result at the top of the third column should be equal to the sum of all the responses and is used to check that the calculations have been performed correctly.

3.0.4.1 Estimating The Effects Of Changing The Variables On The Result

Values of the 'effect' (Eff_i) obtained in this manner provide an indication of the importance of the particular variable i. A high numerical value (either +ve or -ve) of Eff_i indicates that i is a significant variable, a low value that it is not. The estimates obtained of the effect on the result, of changing variable A from a low to a high level is an estimate of the effect of A on the result. For example Eff_A is the difference in responses of any two identical experiments except that, one has 'a' in its TC and the other has not. The value of Eff_a estimated from the third column in Table 3 is the mean of four estimates i.e. a - (1), ab - b, ac - c and abc - bc.

Thus four estimates of Eff_A obtained from a total of eight experiments. Similarly there are four estimates of Eff_B and four estimates of Eff_C, all from the same eight experiments.

In addition, estimates are obtained for the interaction effects between variables, AB, AC, BC, AC and ABC. For example the interaction Eff_{AB} may be defined as the effect of changing the level of A on the effect of B or as the effect of changing the level of B on the effect of A at both low and high C. There are four estimates :–

Effect of level of B on Eff_A :– {ab - b} - {a - (1)} low C

{abc - bc} - {ac - c} high C

Effect of level of A on Eff_B :– {ab - a} - {b - (1)} low C

{abc - ac} - {bc - c} high C

Each of these pairs sums to :– ab - b - a + (1) + abc - bc - ac +c

and as there are four estimates Eff_{AB} = 1/4{ab - b - a + (1) + abc - bc - ac +c} as shown in Table 3.2.

Four estimates of each of the other four interaction effects can be obtained from the same eight experiments in a similar manner.

3.0.4.2 Identifying Significant Effects

It is most important to be able to decide which effects, if any, are of significance, that is likely to be real effects arising from altering variable levels, and not simply caused by experimental error. This can be done graphically [Daniel, C. 1959] for two level factorial analyses. In Daniel's method, the moduli of the effects (i.e. the value of the effect e.g. $4Eff_A/4$, ignoring its positive or negative sign) obtained from the Yates' analysis are plotted in order of increasing magnitude along a linear horizontal axis. The moduli are used, as it is only the magnitude of the effect which is needed, whether that effect is deleterious or beneficial to

the reaction is of no consequence to its significance. The moduli of the effects placed in increasing magnitude on the linear horizontal axis are then projected on to the vertical normal probability axis Pi as shown in Figure 33.

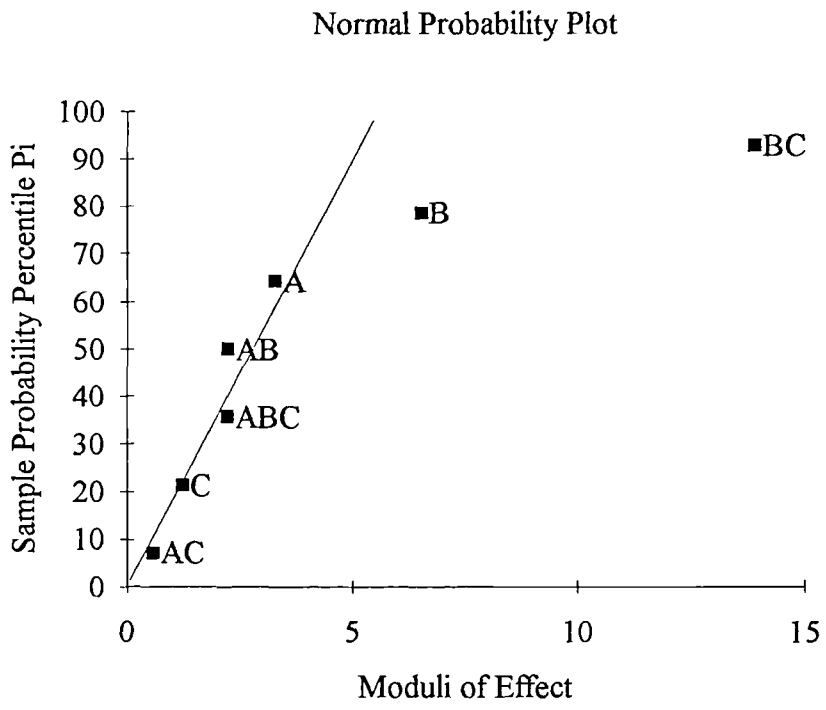


Figure 33 Example Of A Normal Probability Plot Of Effects From A Possible 2^3 Full Factorial Design *

*The probability percentages Pi for successive effects used on a normal probability axis are given by :-

$$Pi = \frac{i - 0.5}{n - 1} . 100\%$$

Where i = 1,2,3....(n-1), n = number of treatment combinations, n-1 = number of factors examined

Hence for a 2^3 full factorial experiment i.e. n = 8,

$$P1 = \frac{0.5}{7} . 100\% = 7.1\%$$

Effects which are not real but due to random experimental error, will fall essentially on a straight line. Those effects which fall 'off it' may be real and deserve further attention. How far from the straight line such points lie is an indication of the magnitude of their effect on the reaction and consequentially the response. For example in Figure 33 only the variable B and the interaction between variables B and C are significant with interaction BC the more so.

In the example, Figure 33 would indicate that the effect of variable B and certainly the interaction effect BC are significant factors as they plot noticeably off the straight line. Chemically plausible explanations can then be sought to explain the significance of particular significant factors and so the researcher can start to formulate ideas about the reaction based on the findings obtained.

The magnitudes of the effects may be used to develop interrelationships between system variables and results via multidimensional plots, commonly star plots generated by a computer. The easiest to understand and utilise for a visual display are three dimensional plots, e.g. Figure 34, showing the major effects of each variable. Such three dimensional interrelationships are known as response surfaces [Montgomery, L.C. 1984]. These functions are useful for analysing problems in which several independent variables influence a dependent variable or response e.g. yield of product. To generate these response surfaces requires the use of sophisticated computer programs, compiling data from factorial analysis and probing analysis of reaction schemes. The response surface can show the presence of maxima (or it could be minima) within the bounds of the variable levels chosen for original factorial design. The maxima can be determined exactly by particular experiments at levels of the system variables within those originally chosen.

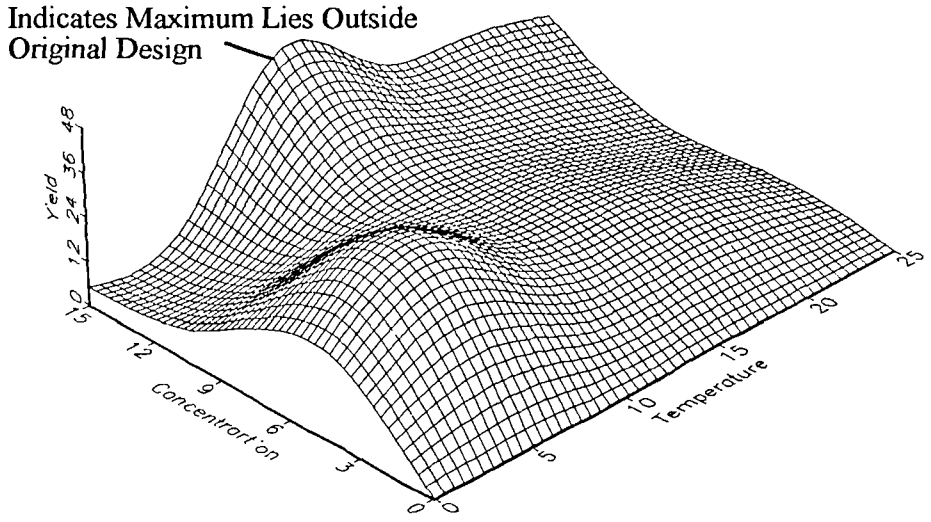


Figure 34 Response Surface Of A Reaction

However the other possibility is that the maximum or minimum (or conceivably more than one) lie outside the original design. Such a possibility is indicated by the response surface shown in Figure 34. In practice, unless the bounds of the original design are very wide apart i.e. there is a very large difference between the low and high levels of the variables, the likelihood is that the second possibility is more likely to arise. Therefore a method of identifying as efficiently as possible where the maximum is located, on the entire response surface with reference to the localised area already defined, is required. Such techniques that are used are known as EVOPS.

3.0.4.3 Multivariable Simplex EVOPS [Box, G.E.P. 1978]

Introduced by G.E.P. Box in 1957, evolutionary operations (EVOPS), was a scheme for deliberately varying the levels of the variables sufficiently for the consequences to be assessed and not yet sufficiently far for those consequences to be significantly harmful to the response i.e

reducing the possibility of 'missing' the maximum. In such a manner the optimum response can be efficiently located. Box used 2^2 factorials as the essential units of his EVOPS i.e four treatment combinations. An approach requiring fewer treatment combinations is that of the simplex EVOP. In this, after an initial 2^3 factorial investigation, unit experiments are designed to exploit the information gained on the significant variables and their interactions from the factorial analysis in order to ascertain where on the entire response surface the maximum is located. The development of a simplex EVOP clearly cannot be done graphically if more than two factors are involved. However a tabular method is available for examining n variables with n+1 treatment combinations, succeeding treatment combinations being constructed in the following manner.

The four treatment combinations giving the best response, i.e. in the case of the response being a yield this would be the four highest yields, are selected from the original factorial analysis. The TC giving the worst (lowest) response is then rejected and the new experimental treatment combination constructed thus :–

i) Sum the levels for each variable in the three remaining TC'S, generating $\sum$ TC.

ii) Calculate the centroid TC of the retained levels = $\{\sum$ TC$\}/3$.

iii) Rejected TC is recovered.

iv) Calculate displacement TC (ii - iii).

v) New TC calculated (ii + iv).

The response of this new TC is then measured, and the process of rejection and the calculation of new TC'S carried out until no further improvement in the response is noted i.e the maximum has been located. Fine tuning, in a sense a return to the classical approach, can be conducted once the optimum in a multivariable system is located. That is to say the effect on the response can measured when one variable is

varied while the others are held at their optimum levels, this procedure can be carried out for each variable in turn. This technique checks that the maximum has been located accurately. In addition it indicates how important deviations from optimum level are for each variable, sharp changes of response indicate variables which must be carefully controlled. When it is necessary to alter the levels of variables, the magnitude of the change for each variable is up to the experimenter, and the size of the change is not critical if the later experiments can be expanded or contracted as required, as the investigation proceeds.

3.0.5 Fractional Factorial Analysis

In situations where factorial investigations of the chosen variables has failed to increase the response to the desired level e.g. the product yield is still well below 100%, the experimenter is forced to consider what other variables are affecting the response, since the variables selected do not encompass all the significant variables that govern the reaction. In such a case, one must fall back to an empirical understanding of the reaction and utilise the information on significant factors gained from the initial factorial investigation in deciding further variables for investigation.

Fractional factorial experiments are the most economical method of assessing the importance of a number of system variables and some of their interactions, when there is some knowledge of variable significance obtained from previous experiments. In order to assess seven variables by the factorial method, the experimenter would have to carry out at least 2^6 = 64 experiments. Every factorial design is said to have a set of n+1 multipliers, so for a 2^6 design with variables A, B, C, D, E & F these are (1), a, b, c, d, e, & f. To derive the list of treatment combinations, begin

with (1) at the top and multiply the list algebraically by each successive multiplier, thus generating a successively larger list after each multiplication. So multiplying (1) by 'a' yields 'a', now multiplying both (1) and 'a' by 'b' yields 'b' and 'ab', working similarly through to 'f ' yields the full set of treatment combinations in the order required for Yates' analysis :– (1), a, b, ab, c, ac, bc, abc, d, ad, bd, abd, cd, acd, bcd, abcd, e, ae, be, abe, ce, ace, bce, abce, de, ade, bde, abde, cde, acde, bcde, abcde, f, af, bf, abf, cf, acf, bcf, abcf, df, adf, bdf, abdf, cdf, acdf, bcdf, abcdf, ef, aef, bef, abef, cef, acef, bcef, abcef, def, adef, bdef, abdef, cdef, acdef, bcdef, abcdef. This method may be used to derive any full set of treatment combinations and in the order demanded by the Yates' analysis. The fractional factorial approach attempts to reduce the number of experiments required by dividing the full factorial into 8 blocks of 16 individual experiments, so as to include the variables and variable interactions which are believed to be of most importance in the first one or two blocks. If the choice proves to be correct only one or two blocks need be performed to obtain the relevant information. Remembering that for a 2^7 factorial most of the effects estimated would be of high order interactions, which could possibly be negligible or in any case incomprehensible, with forethought and prior knowledge of at least some of the significant factors, the choice of possible important variables and variable interactions is easier than it first appears to be. However there are certain pitfalls which should be avoided and others to be aware of. An example of the pitfalls associated with fractional factorial design is described below.

Consider a 2^3 experiment which is divided into two blocks of four treatment combinations, this introduces another source of possible variation, there may be some systematic difference between the blocks e.g. different operators, different source of raw material, etc. So, this between blocks difference becomes confounded (i.e. mixed up), with one of the

seven effects of the 2^3 design and so the subdivision causes the experimenter to lose all knowledge of the magnitude of one of the effects. For example, consider a 2^3 experiment which is divided between two batches of the same raw material or reactant :–

Batch 1 : a, ab, ac, abc

Batch 2 : (1), b, c, bc

and suppose the raw material in Batch 1 has a superior quality, e.g. less impurities, to that in Batch 2. The effect of A, as observed, equals the true effect of A plus the effect of any difference between batches. Since the effect of the difference is not known, the true effect of A cannot be known, that is the effect of A is confounded (i.e. mixed up) with another effect, in this case the difference between the batches. There is no knowledge of the importance of A because the two batches of raw material were not randomly distributed across the two blocks. Similar confounding would occur if two operators or two chemical plants were assigned to the two blocks respectively.

Whenever a factorial experiment is divided into blocks, one or more effects are confounded with the between blocks difference, which will always remain unknown, and the true magnitude of these effects cannot be known. Clearly it is advisable to confound the least important effect. The rule to follow is that significance is likely to decrease as the order of the interaction increases. This does not always hold for three fold interactions, i.e. ABC. Generally speaking it is recommended to include at least five variables in a fractional factorial experiment i.e. only fractional factorials of 2^5 factorials or higher should be investigated. In such a case, the highest interaction effect is ABCDE and it is likely to be zero, though this can lead to unforeseen complications in designing the blocks.

There are consequences of choosing the effects to confound with the between blocks difference. It can be shown that, when confounding a 2^n factorial into 2^p blocks, p interactions or factors can be chosen to be confounded and another 2^p - p - 1 factors or interactions are also confounded. For example dividing a 2^6 factorial into 2^3 blocks requires that three factors or interactions are chosen to be confounded, another 2^3 - 3 -1 = 4 factors or interactions will also be confounded. The chosen three factors or interactions are called the "defining contrasts" of the design, the other four factors or interactions are termed "generalised interactions" and no information can be obtained about them. To illustrate, consider that the variables are A, B, C, D, E & F and the defining contrasts are chosen to be ABCDEF, ABCDE & ABCDF. The four generalised interactions are obtained by algebraic multiplication of the four combinations of the defining contrasts, counting squared terms as unity, thus

ABCDEF. ABCDE = F

ABCDEF. ABCDF = E

ABCDE. ABCDF = EF

ABCDEF. ABCDE. ABCDF = ABCD

This is therefore a poor design if E and F are important variables, since no information can be obtained about them. If they are not anticipated as possibly important then why include them in the design initially ? This is a clear example of the inadvisability of using highest and next highest interactions as defining contrasts in multi–block designs, as main effects become confounded. It is best to choose medium order interactions, so that no main effects are confounded and the confounded interactions are probably of little importance. The selection of these defining contrasts is therefore of crucial importance, more so when it is

remembered that it is intended that not all the blocks of the factorial are going to be completed, in the case of a fractional factorial investigation.

In designing fractional factorials, the experimenter has the intention of completing only the experiments in one or two blocks. Whilst any block may be chosen at random (and further blocks may subsequently be completed), it is often necessary to do the principal block first. The principal block is that block which includes the treatment combination (1), as it includes all variables at a low level. The standard method to derive the principal block is to assimilate all the treatment combinations which have zero, 2, 4 ..... letters in common with each of the defining contrasts and place them in the principal block. The remaining blocks of a fractional factorial design are derived by multiplying, algebraically as before, the contents of the principal block successively by elements not in that block nor in any block already formed. This is illustrated in Table 3.3.

Table 3.3 Fractional Factorial Blocks Of A 2^6 Factorial

Principal Block 1	Block 2 1 x a	Block 3 1 x e	Block 4 1 x f	Block 5 1 x ae	Block 6 1 x af	Block 7 1 x ef	Block 8 1 x aef
(1)	a	e	f	ae	af	ef	aef
ab	b	abe	abf	be	bf	abef	bef
ac	c	ace	acf	ce	cf	acef	cef
bc	abc	bce	bcf	abce	abcf	bcef	abcef
ad	d	ade	adf	de	df	adef	def
bd	abd	bde	bdf	abde	abdf	bdef	abdef
cd	acd	cde	cdf	acde	acdf	cdef	acdef
abcd	bcd	abcde	abcdf	bcde	bcdf	abcdef	bcdef

The lower case letters denote treatment combinations.

For the 2^6 experiment in 2^3 blocks, with ABCDEF, ABCDE and ABCDF as defining contrasts, the treatment combinations with 0, 2, 4 letters in common with each of these interactions form the principal block. The other seven blocks arise via the multiplicative procedure described.

The full design presented in Table 3.3 shows why no estimate of the effect of E or F can be obtained as no block has a mixture of levels of either E or F i.e. e and f do not appear together in the same block.

A valid design to estimate the effect of each main variable will always have in each block, for any main variable which appears in the block, half the treatment combinations at a high level and the other at low levels.

If only one block is investigated in a fractional factorial experiment, additional information is lost in addition to the confounded effects. What actually happens is that each effect corresponding to the treatment combinations of that block become aliased to seven other effects i.e. the treatment combinations of the principal block become associated with certain other effects. This aliasing or association with other effects occurs as a result of the generalised interactions of the principal block effects with the confounded effects (defining contrasts) and the confounded effects' generalised interactions. This is illustrated in Table 3.4.

Table 3.4 Aliases Of Effects In Principal Block Of 2^6 Fractional Factorial

Principal Block 1	Aliases Generated By Confounded Effects				Aliases Generated By Generalised Interactions		
I	ABCDEF	ABCDE	ABCDF	-E	-F	EF	ABCD
AB	CDEF	-CDE	-CDF	-ABE	-ABF	ABEF	CD
AC	BDEF	-BDE	-BDF	-ACE	-ACF	ACEF	BD
BC	ADEF	-ADE	-ADF	-BCE	-BCF	BCEF	AD
AD	BCEF	-BCE	-BCF	-ADE	-ADF	ADEF	BC
BD	ACEF	-ACE	-ACF	-BDE	-BDF	BDEF	AC
CD	ABEF	-ABE	-ABF	-CDE	-CDF	CDEF	AB
ABCD	EF	-E	-F	-ABCDE	-ABCDF	ABCDEF	I

The upper case letters denote effects.

Here, for the principal block of the 2^6 fractional factorial design, the effects investigated are aliased (associated) to those effects generated (i.e. multiplying algebraically the effects investigated), by all the three confounded effects and the four generalised interactions. Note that where an effect is multiplied by a confounded effect or generalised interaction containing an odd number of letters the result is negative. The poor design of this fractional factorial is readily apparent, since there is aliasing between two factor interactions e.g. Effect of AB = Effect of CD and Effect of AC = Effect of BD and Effect of AC = - Effect of ACE and Effect of AB = - Effect of CDE.

Since the allocation of treatment combinations to blocks and the aliasing of effects depend on the choice of the defining contrasts, their selection is of primary importance. The design of the principal block of the fractional factorial must allow the effects expected to be significant, to be

aliased to effects which are expected to be insignificant. There are two ways to select the defining contrasts, the first being to consult a set of published designs [Davies, O.L. 1954], which outlines consequences of certain sets of defining contrasts. However this textbook can offer no guidance as to the selection of defining contrasts with regard to the experimental objectives other than by trial and error. An improved method [Franklin, M. 1977] based on a systematic approach first suggested by Greenfield in 1976 will now be demonstrated.

Consider a 2^5 factorial experiment with variables A, B, C, D & E, a design is required which will investigate each main effect and also the interaction effects AB and BE. The set of effects to be investigated is termed the requirements set. To estimate the seven (n) effects requires eight (n+1) experiments, and so of the $2^5 = 32$ possible TC'S, at least $8 = 2^3$ are required. Therefore, a four (2^2) block fractional factorial design of a 2^5 factorial will suffice, having two defining contrasts and one generalised interaction. It is unwise to design blocks of less than eight treatment combinations in multi-factor fractional designs as aliasing becomes rampant. A 2^3 design is required for a full factorial investigation of three factors A, B and C. In designing the principal block to analyse the requirement set, these three factors are called the basic factors and D and E are the added factors; in general n-m basic factors, where n = N°. of variables and m = added factors. Identification of appropriate defining contrasts begins by constructing a table with the eight effects of the full 2^3 factorial (the basic factors) placed vertically in the Yates' analysis order (see Table 3.2) and the two added factors placed horizontally as shown in Table 3.5.

Table 3.5 Eligible Effects For Fractional Design Of 2^5 Factorial With Chosen Requirement Set : A, B, C, D, E, AB & BE

Basic Effects	Added Factors →	
↓	D	E
I	D✗	E✗
A	AD✗	AE✗
B	BD✗	BE✗
AB	ABD✗	ABE✗
C	CD✗	CE✗
AC	**ACD**	**ACE**
BC	**BCD**	BCE✗
ABC	**ABCD**	**ABCE**

✗ Ineligible effects

None of the requirement set may be used as defining contrasts obviously, and it is necessary to distinguish between eligible effects which may be selected as defining contrasts, and ineligible effects which may not. For a given requirement set, all the effects in that set are ineligible for selection as defining contrasts and their generalised interactions between pairs in that set, and the zero effect I, corresponding to the mean of all the experimental results. So for the requirement set A, B, C, D, E, AB and BE the ineligible set is I, A, B, AB, C, AC, BC, ABC (the basic factors) and D, AD, BD, ABD, CD, E, AE, BE, ABE, CE, BCE, DE, and BDE.

To find the two defining contrasts and their generalised interaction which are not in the ineligible set, the basic effects are multiplied by the added factors (see Table 3.5) and those within the ineligible set are deleted. The first eligible effect in the first added factors column, ACD, is

selected, then the second column is searched for any eligible effect whose generalised interaction with ACD is also eligible. Neither ACD. ACE = DE nor ACD. ABCE = BDE are eligible (squared terms counted as unity). The next eligible effect BCD in the first column is therefore selected and the second column searched. Both BCD. ACE = ABDE and BCD. ABCE = ADE are eligible and the final effect ABCD is also eligible. There are therefore two sets of three eligible effects ACE, BCD, ABDE and ADE, BCD, ABCE and either will suffice. The principal block containing the eight treatment combinations is derived from the total set by the normal method (TC'S with 0, 2, 4 .... letters in common with each of the defining contrasts).

The principal block is therefore composed of I, ABC, BD, ACD, AE, BCE, ABDE, CDE, but they must be placed in the Yates' analysis order i.e. I, AE, BD, ABDE, CDE, ACD, BCE, ABC (as for the basic factors it is I, A, B, AB, C, AC, BC, ABC). The aliasing matrix will indicate which effects are aliased with one another and which row of the Yates' table gives which effect. The aliasing matrix is obtained by multiplying the principal block for a 2^3 full factorial experiment (in general for a full factorial in the basic factors) successively by the defining contrasts and their generalised interaction as shown in Table 3.6. The required effects are in bold, the negative signs arising from the rule governed by the number of letters in the defining contrast. So this matrix indicates which effects are aliased with the required effects e.g. Effect of E = - Effect of AC, and the order in which the required effects appear in the Yates' analysis table.

Table 3.6 Aliasing Matrix For Fractional Design Of 2^5 Factorial With Chosen Requirement Set : A, B, C, D, E, AB & BE

Basic Factors	xACE	xBCD	xABDE
I	-ACE	-BCD	ABDE
A	-CE	-ABCD	BDE
B	-ABCE	-CD	ADE
AB	-BCE	-ACD	DE
C	-AE	-BD	ABCDE
AC	**-E**	-ABD	BCDE
BC	-ABE	**-D**	ACDE
ABC	**-BE**	-AD	CDE

The order in the Yates' analysis table for the treatment combinations was (1), ae, bd, abde, cde, acd, bce & abc and the corresponding effects are I, $4Eff_A$, $4Eff_B$, $4Eff_{AB}$, $4Eff_C$, $-4Eff_E$, $-4Eff_D$ & $-4Eff_{BE}$, remembering that the factor 4 arises from the calculations performed within the Yates' table. The design assumes that the aliases are negligible, but in real terms it must be remembered that certain two factor interactions can be real chemical interactions. In the end, it is up to the chemist to use this tool with forethought and full awareness of its limitations.

3.1 Multivariate Optimisation Of 1–Methoxy–3–Methyl–2–Phospholene Oxide Synthesis

As explained in the previous section, to apply this technique, firstly, one selects the variables which are believed to govern the experiment, based on the available background knowledge to the reaction and/or from actual experimental results. For this particular reaction, the variables selected were reaction temperature, concentration of 1,1,1–trichloro –3–methyl–3–phospholene and addition time of the methanol. These variables were chosen based on the information obtained from the previous initial attempts to optimise the reaction by using classical methods (see section 2.3). The reaction was also to be carried out under acidic conditions, that is no triethylamine and therefore no precipitate problem due to triethylammonium chloride formation. The information obtained from the analysis would indicate which of these three selected variables were important and then other variables could be altered in the reaction, if it proved necessary to optimise further. These other variables that might affect the overall yield were pre– and post mixing times, temperature for pre– and post mixing and solvent choice. To include them in the initial investigation would needlessly complicate the preliminary experiments and make the interpretation of results very complex.

Recalling the section on Chemometrics, a high and low value for each variable was then selected, the values being based on information obtained in the initial attempts to optimise the reaction by using classical methods. For a full factorial investigating three variables there are eight (2^3) different experimental conditions with the variables at their high and low levels. These experiments were performed in random order to irradicate confusion of correlation with causation and the raw data (experimental percentage yield) processed in a pre–specified order. From

the design of the experiment, four estimates of the effects of the variables and variable interaction effects were obtained. For the Stage II synthesis, the three defined variables and their levels were :—

A) Temperature of cooling bath, -15°C (low level) or 0°C (high level).

B) Concentration of 1,1,1–trichloro–3–methyl–3–phospholene in methylene chloride, 50g in 400 mls (low level) or 100g in 400 mls.

C) Addition time for 68 mls of methanol, 1 Hr (low level) or 4 Hrs (high level).

Each individual experiment or treatment combination is expressed in shorthand notation as described in section 3.0.4 (if the lower case letter of the assigned variable is present it infers that the variable is at its high value, if it is absent, the variable is at its low level, i.e. ac means high level of a, low level of b and high level of c; (1) means low level of a, low level of b and low level of c). The experimental procedure for the treatment combinations is outlined below and then the responses for any one treatment combination are given in Table 3.7.

To 400 mls of methylene chloride was added either 50g (0.25 moles) or 100g (0.5 moles) of 1,1,1–trichloro–3–methyl–3–phospholene (synthesised as described in section 2.2) and the mixture stirred at either 0°C or -15°C under a flowing atmosphere of nitrogen. Distilled methanol 68 mls (1.5 moles) was then slowly added over either one or four hours, keeping the temperature at its previous level. At the end of the addition, the solution was brought to room temperature (25°C) and stirred for a further two hours. The hydrogen chloride gas evolved during the reaction

was passed through a potassium hydroxide scrubber to remove it. The solution was then neutralised with saturated sodium hydrogen carbonate solution. The methylene chloride layer was separated and the aqueous layer extracted with methylene chloride (5 x 100 mls). The organic layers were then recombined and the solvent removed on a rotary evaporator, leaving the required product as a red orange oil.

Table 3.7 Responses From Stage II Treatment Combinations

Treatment Combination	Response (Percentage Yield)
(1)	24.8
a	42.5
b	39.0
ab	18.2
c	32.8
ac	33.0
bc	13.2
abc	24.3

Subsequent analysis of the data, in this order via a Yates' table produced the results seen in Table 3.8.

Table 3.8 Yates' Analysis Of Percentage Yield From Treatment Combinations For Stage II Given In Table 3.7

Response	1	2	3	Effect
24.8	67.3	124.5	227.8 = Sum of Responses	—
42.5	57.2	103.3	$8.2 = 4eff_a$	2.05
39.0	65.8	-3.1	$-38.4 = 4eff_b$	-9.6
18.2	37.5	11.3	$-27.6 = 4eff_{ab}$	-6.9
32.8	17.7	-10.1	$-21.2 = 4eff_c$	-5.3
33.0	-20.8	-28.3	$14.4 = 4eff_{ac}$	3.6
13.2	0.2	-38.5	$18.2 = 4eff_{bc}$	4.55
24.3	11.1	10.9	$49.4 = 4eff_{abc}$	12.35

Thus, Effect of A = 2.05 (Temperature effect)

Effect of B = -9.6 (Concentration effect)

Effect of C = -5.3 (Time effect)

Interaction Effects :—

Effect of A on B on C = 12.35 (Threefold interaction effect)

Effect of A on C = 3.6 (Temperature/Time interaction effect)

Effect of A on B = -6.9 (Temperature/Concentration effect)

Effect of B on C = 4.55 (Concentration/Time effect)

The modulus of the effects (whether an effect is advantageous or detrimental, inferred by the + or - signs, is not in question, but the size of the effect pertains to its significance on the reaction) are then plotted on a probability graph to determine their significance. The modulus of each

effect is placed in ascending order on the x–axis and then projected on to the y–axis, based on their statistical probability (see Figure 35).

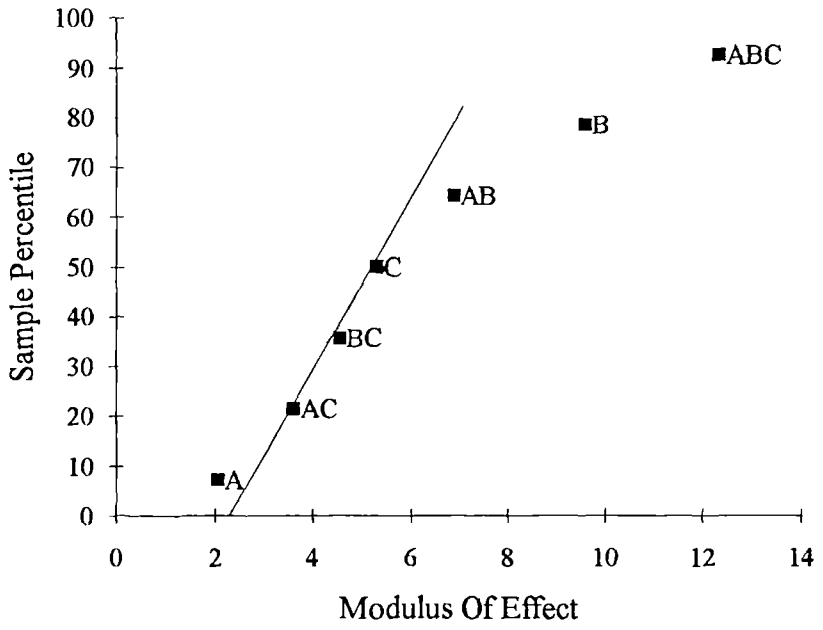


Figure 35 Normal Probability Plot Of Variable Effects

By convention, in such a plot, those effects which are not significant but due to random (i.e. experimental) error, will plot essentially on a straight line. Those effects which fall 'off it' may be significant and deserve further attention. Where there are many significant effects, there may be difficulty in deciding which straight line is the best one. Firstly, as a rule of thumb, the straight line incorporating the most points having small effects is taken in favour of one which contains points having larger effects, since larger effects are more likely to be of significant and not due to random error. Secondly, and more importantly, a reverse Yates calculation [Box, G.E.P. 1969] can be performed to identify true significant effects. In Figure 35, it is possible to draw two straight lines, the solid line being more favourable as it 'fits' to more points. However,

the solid line implies that variable A is significant, whereas the dotted line suggests otherwise. This can be further clarified by a reverse Yates calculation. The principle of a reverse Yates calculation is simple, if some effects are 'noise' i.e. not significant, then the estimates gained of them should really be zero. By writing down the results (4 x effects) from a factorial design in reverse Yates order, which includes zero values for any effects which appear unreal i.e. are not significant from the normal probability plot, and then carrying out the normal addition and subtraction in pairs, will generate calculated responses which can be compared to the actual responses. Therefore, from the normal probability plot, the solid line implies AC, BC and C are not significant and the dotted line implies A, BC and AB are not significant. To check the validity of each of these lines, reverse Yates calculations were performed. For the solid line , writing down the results from Table 3.8 column 3 in reverse Yates order , giving zero values to effects AC, BC and C as they are assumed not to be significant, then performing the Yates calculation generates the figures seen in Table 3.9. The actual experimental responses Y from Table 3.7 (but in reverse order) are then subtracted from the calculated responses y in Table 3.9 (column 3 ÷8). The eight residuals generated are then plotted on a probability scale, if the effects assumed to be zero are not in fact significant, then the responses which estimate those effects, and hence the residuals generated, will lie on a straight line, since they are in effect due to experimental error i.e. random, and unaffected by those variable effects. Those effects that are significant will lie 'off' this straight line. If this is not the case, then the assumption is wrong. The total sum of responses, opposite the treatment combination (1) in the Yates table of analysis, is a non–existent or zero effect corresponding to the mean of all the experimental results. Figure 36 shows the probability plot of the residuals generated in Table 3.9. It can

be clearly seen that the effects assumed not to be significant are in actual fact not significant as they still lie on a straight line and therefore the solid line is the genuine line on Figure 35. To further confirm this, reverse Yates calculations assuming effect A is not significant as well as effects AC, BC and C and reverse Yates calculations for the effects on the dotted line were also performed.

Table 3.9 Reverse Yates Calculation, Assuming AC, BC And C Are Not Significant

Responses Reversed	Reverse Order	1	2	3	Calculated Response y	Actual Response Y	Residual Y - y
49.4 = $4eff_{abc}$	49.4	49.4	49.4	219.4	27.425	24.3	-3.125
18.2 = $4eff_{bc}$	0*	0	170	159.4	19.925	13.2	-6.725
14.4 = $4eff_{ac}$	0*	-66	-49.4	252.6	31.575	33	1.425
-21.2 = $4eff_{c}$	0*	236	208.8	279.8	34.975	32.8	-2.175
-27.6 = $4eff_{ab}$	-27.6	-49.4	-49.4	120.6	15.075	18.2	3.125
-38.4 = $4eff_{b}$	-38.4	0	302	258.2	32.275	39	6.725
8.2 = $4eff_{a}$	8.2	-10.8	49.4	351.4	43.925	42.5	-1.425
227.8 = Sum of Responses	227.8	219.6	230.4	181	22.625	24.8	2.175

* Assumed not to be significant, ∴ value replaced by zero.

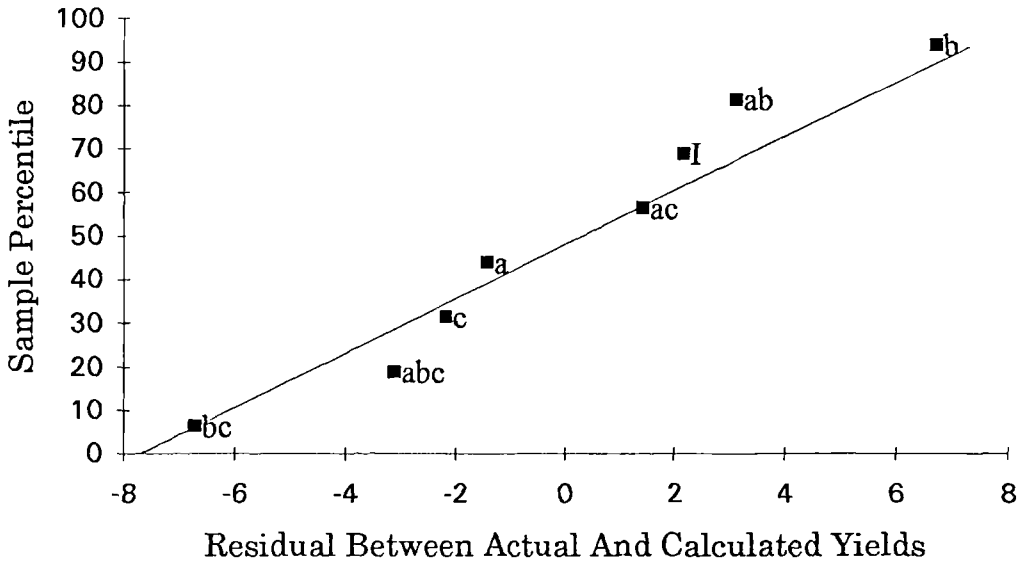


Figure 36 Reverse Yates Normal Probability Plot Assuming Variable Effects AC, BC And C Are Not Significant

Table 3.10 Reverse Yates Calculation, Assuming A, AC, BC And C Are Not Significant

Responses Reversed	Reverse Order	1	2	3	Calculated Response Y	Actual Response y	Residual Y - y
$49.4 = 4eff_{abc}$	49.4	49.4	49.4	211.2	26.4	24.3	-2.1
$18.2 = 4eff_{bc}$	0*	0	161.8	167.6	20.95	13.2	-7.75
$14.4 = 4eff_{ac}$	0*	-66	-49.4	244.4	30.55	33	2.45
$-21.2 = 4eff_{c}$	0*	227.8	217	288	36	32.8	-3.2
$-27.6 = 4eff_{ab}$	-27.6	-49.4	-49.4	112.4	14.05	18.2	4.15
$-38.4 = 4eff_{b}$	-38.4	0	293.8	266.4	33.3	39	5.7
$8.2 = 4eff_{a}$	0*	-10.8	49.4	343.2	42.9	42.5	-0.4
227.8 = Sum of Responses	227.8	227.8	238.6	189.2	23.65	24.8	1.15

* Assumed not to be significant, ∴ value replaced by zero.

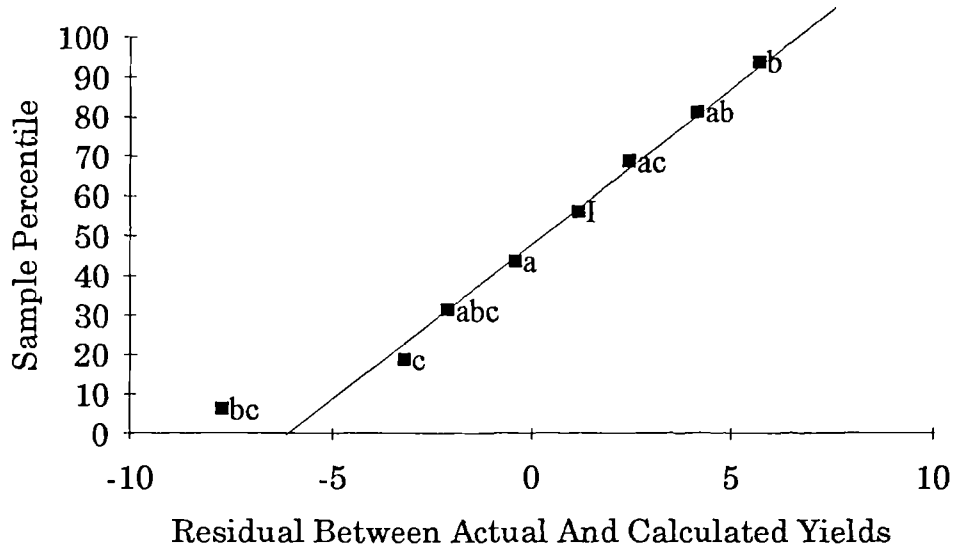


Figure 37 Reverse Yates Normal Probability Plot Assuming Variable Effects A, AC, BC And C Are Not Significant

Table 3.11 Reverse Yates Calculation, Assuming A, BC And AB Are Not Significant (Dotted Line In Figure 35)

Responses Reversed	Reverse Order	1	2	3	Calculated Response Y	Actual Response y	Residual Y - y
$49.4 - 4eff_{abc}$	49.4	49.4	42.6	232	29	24.3	-4.7
$18.2 = 4eff_{bc}$	0*	-6.8	189.4	104.4	13.05	13.2	0.15
$14.4 = 4eff_{ac}$	14.4	-38.4	-85	210	26.25	33	6.75
$-21.2 = 4eff_{c}$	-21.2	227.8	189.4	280	35	32.8	-2.2
$-27.6 = 4eff_{ab}$	0*	-49.4	-56.2	146.8	18.35	18.2	-0.15
$-38.4 - 4eff_{b}$	-38.4	-35.6	266.2	274.4	34.3	39	4.7
$8.2 = 4eff_{a}$	0*	-38.4	13.8	322.4	40.3	42.5	2.2
227.8 = Sum of Responses	227.8	227.8	266.2	252.4	31.55	24.8	-6.75

* Assumed not to be significant, ∴ value replaced by zero.

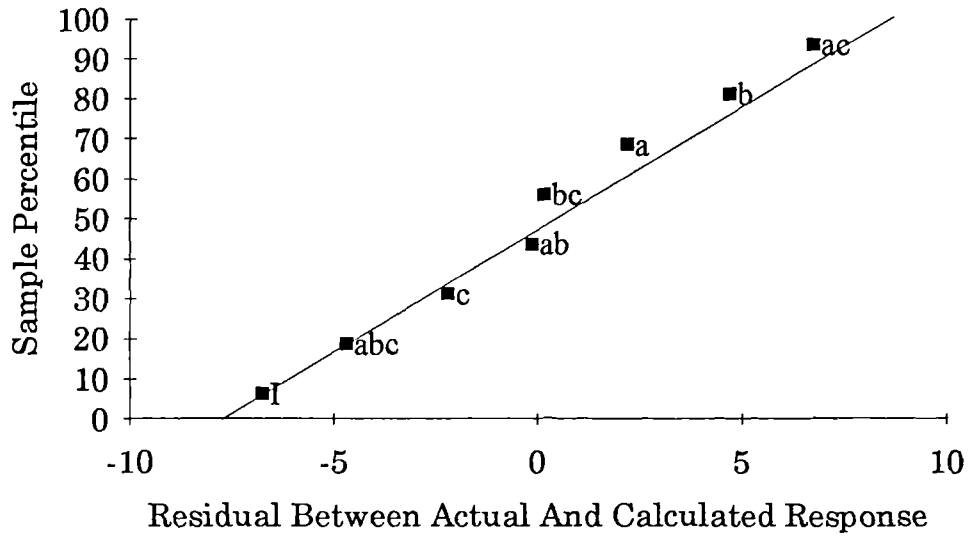


Figure 38 Reverse Yates Normal Probability Plot Assuming A, BC And AB Are Not Significant

Figure 37 illustrates the result of assuming that the effect of A in addition to the effects of AC, BC and C, is not significant. Not all of the residuals calculated from the assumed non–significant effects lie on a straight line and therefore the assumption is incorrect. Also most of the significant effects lie on this line, and therefore it is false to assume that the effect of variable A is not significant. Figure 38 illustrates the result of assuming that the effects of A, BC and AB (Dotted line in Figure 35) are not significant. The three calculated residuals from the assumed non–significant effect do not lie on a straight line. Thus by analysing the data points from Figure 35 via the reverse Yates method, has strengthened initial inferences, and has prevented any false assumptions of non–significance.

Therefore, from Figure 35, the significant effects in ascending order of importance are :—

A : The effect of Temperature.

AB : The interaction effect between Temperature and Concentration.

B : The effect of Concentration of 1,1,1–trichloro–3–methyl–3–phospholene in methylene chloride.

ABC : The threefold interaction effect between Temperature, Concentration and Addition Time.

The interaction effect AB may be defined as the effect of the level of variable B on the effect of variable A or vice versa. Normally, threefold interactions are negligible, however in this case, it is the most significant effect. Unfortunately it is almost impossible to visualise the effect of changing temperature on changing concentration on changing addition time in a physical sense and therefore difficult to utilise its effect, as a change in any the three system variables will result in the consequential threefold interaction effect being more important. This information is however, vital in deciphering experimental results in a meaningful fashion. The concentration effect (-ve) is highly significant and infers that decreasing the concentration will increase the yield. The temperature with concentration interaction effect (-ve) infers that decreasing the temperature will decrease its importance on the effect of concentration and therefore increase the yield if lower concentrations are used, as supported by the inferences of the effect of concentration. Therefore the temperature/concentration combination needs to be optimised. Finally the temperature effect (+ve) infers that increasing the temperature slightly should result in an improved yield, this effect is in opposition to the two fold interaction effect of temperature with concentration. The effect of the addition time of methanol or any of its interaction effects, excepting the threefold interaction effect, appear to have no significance and so the time can be reduced.

So having identified the important effects within the chosen parameters, a set of probing experiments can be conducted to verify the findings from the initial factorial and then new experiments can be performed with parameters changed, as dictated by the concluded significant effects, to further increase the yield. From the initial full factorial, the three highest yields obtained were 42.5%, 39% and 33% from treatment combinations a, b and ac respectively. These three sets of reaction conditions are :—

i) A temperature of 0°C, a concentration of 50g of 1,1,1–trichloro–3–methyl–3–phospholene in 400mls methylene chloride and a one hour addition time of methanol to give a 42.5% yield.

ii) A temperature of -15°C, a concentration of 100g of 1,1,1–trichloro–3–methyl–3–phospholene in 400mls methylene chloride and a one hour addition time of methanol to give a 39% yield.

iii) A temperature of 0°C, a concentration of 50g of 1,1,1–trichloro–3–methyl–3–phospholene in 400mls methylene chloride and a four hour addition time of methanol to give a 33% yield.

By completing exploratory experiments, three dimensional plots (response surfaces) were then constructed to illustrate the importance of the threefold interaction and to ascertain if a maximum yield occurred within the chosen values of the variables. The two response surfaces at low and high addition times shown in Figures 39 and 40 respectively, demonstrate the importance of the three fold interaction ABC.

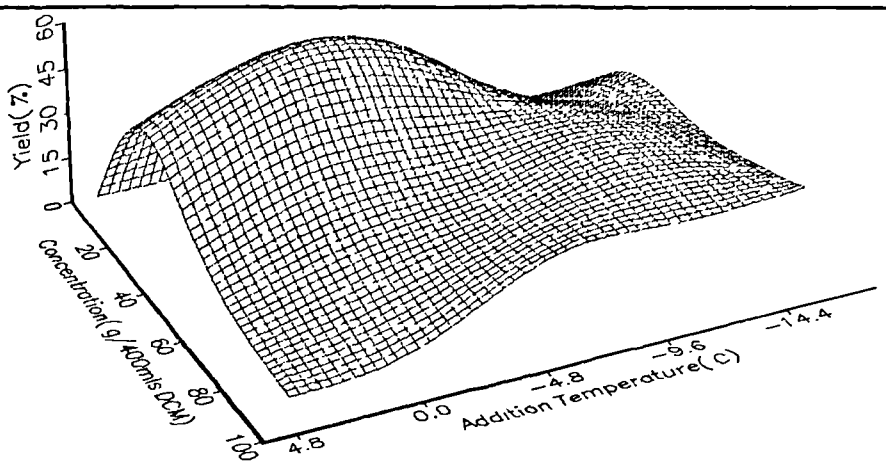


Figure 39 Low Addition Time 3D Response Surface

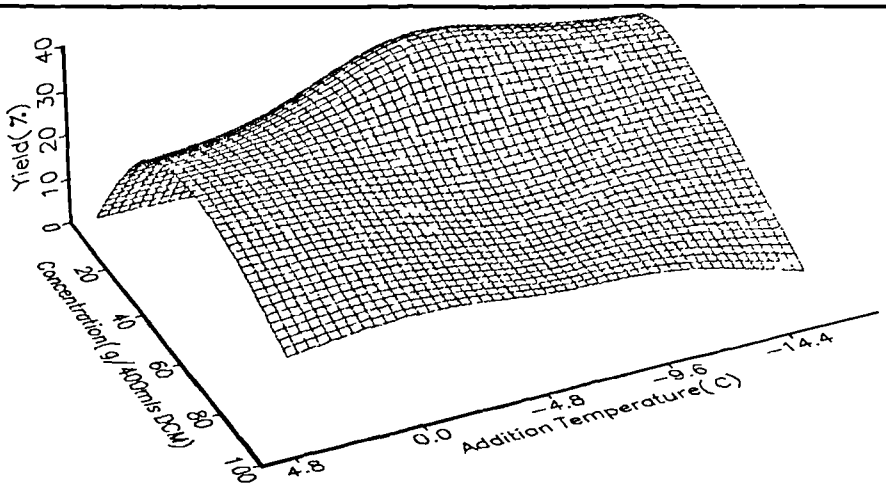


Figure 40 High Addition Time 3D Response Surface

The complex surfaces, depicting concentration and addition temperature relationships, change dramatically between the low and high addition times i.e the surface's relationship with addition time is significant (interaction ABC). The fact that a maximum (ca. 50%) occurs on the low addition time response surface (see Figure 39) suggests that extra variables will need to be investigated in order to increase the yield further.

3.2 Further Optimisation Of 1–Methoxy–3–Methyl–2–Phospholene Oxide Synthesis Using Fractional Factorials

Following multivariate simplex EVOPS designs a new treatment combination (probing experiment) was produced by selecting the four treatment combinations that gave the best responses (i.e yields), rejecting the worst of these and then calculating the new treatment combination. This is also regulated by the known variable effects generated i.e. since the concentration effect is negative then concentration should be lowered, also the addition time of methanol should be reduced, but the quantity of methanol was increased to note its effect. The temperature was maintained at its previous level due to the disparity between the temperature effect and the interaction of temperature with concentration. The new probing experiment generated had the variables set at the levels, temperature 0°C, concentration of 1,1,1–trichloro–3–methyl–3–phospholene being 25g in 400 mls methylene chloride, 136 mls of methanol added over half an hour. The remainder of the experiment was as before. The yield was recorded as 57%, a significant increase over the previous highest yield of 42.5%. The multivariate simplex EVOPS exercise was used to generate sequentially three more experiments, with only one variable altered, two with temperatures of +5°C and -5°C and one with the stirring time halved to one hour. These experiments gave yields of 42%, 51% and 54% respectively, all lower than the 57% level achieved earlier. In utilising multivariate simplex EVOPS, it is essential to utilise previously gained knowledge to modify or disregard the statistically generated conditions; any statistical design in chemistry must use both the principles of statistics and those of chemistry.

These results and that implied by the response surface in Figure 39 suggested that other factors were also significantly affecting the yield and

needed to be investigated in order to increase the yield still further. By looking at the entire experimental process that gave a 57% yield and using the additional information already obtained, further variables that might affect the yield were identified for subsequent investigation. Five variables were selected and a fractional factorial analysis performed, which had been designed to reduce the number of experiments needed to produce the relevant information. These variables selected included two 'old' variables of addition temperature and methanol addition time, since it was felt that the interaction effects between 'new' and these 'old' variables would be significant. In performing a fractional factorial, certain effects will be lost, but by careful design, the effects lost can be selected to be those reckoned to be of least significance. It is also important to note that the effects of the variables investigated by performing only the principal block will be aliased (i.e. mixed up) with certain two factor interaction, as described in an earlier section (3.0.5). If further information is required or the significance of aliases needs to distinguished , then the relevant block could be performed. The five variables selected were :—

A) Addition Temperature, -10°C (low level) or 0°C (high level).

B) Addition Time Of Methanol, 15 minutes (low level) or 30 minutes (high level).

C) Quantity Of Methanol, 136 mls (low level) or 272 mls (high level).

D) Stirring Time After Addition, ½ Hr (low level) or 2 Hrs (high level).

E) Stirring Temperature, addition temperature {i.e. no change} (low level) or room temperature {25°C} (high level).

The principal block was designed to provide estimates of the effects of addition temperature, methanol addition time, stirring time, quantity of methanol , addition temperature with quantity of methanol interaction (aliased with – stirring time and stirring temperature interaction), stirring temperature and addition temperature with stirring time interaction (aliased with quantity of methanol and stirring time interaction). The design was accomplished in the following manner (described in detail in section 3.0.5).

In dividing a 2^5 factorial into 4 blocks of 8 experiments, two effects will be confounded and a third effect will be their generalised interaction. The designated effects, called the requirement set of effects, to be estimated was A, B, C, D, E, AC and AE.

Table 3.12 Eligible Effects For Fractional Design Of 2^5 Factorial With Chosen Requirement Set : A, B, C, D, E, AC & AE

Basic Effects	Added Factors →	
↓	D	E
I	D✗	E✗
A	AD✗	AE✗
B	BD✗	BE✗
AB	ABD✗	ABE✗
C	CD✗	CE✗
AC	**ACD**	**ACE**
BC	**BCD**	BCE✗
ABC	**ABCD**	**ABCE**

✗ Ineligible Effects

ABD and BCE selected as defining contrasts, ACDE being their generalised interaction. The aliasing matrix indicates which effects are aliased with one another and which row of the Yates' table gives which effect (see Table 3.13).

From Table 3.13, there is aliasing of B with -AD & -CE
AC with DE and A with -BD
AE with CD and E with -BC
C with -BE and D with -AB

Table 3.13 Aliasing Matrix For Fractional Design Of 2^5 Factorial With Chosen Requirement Set : A, B, C, D, E, AC & AE

Basic Factors	xABD	xBCE	xACDE	Effect
I	-ABD	-BCE	ACDE	4 x Average
A	-BD	-ABCE	CDE	$4Eff_A$
B	-AD	-CE	ABCDE	$4Eff_B$
AB	**-D**	-ACE	BCDE	$-4Eff_D$
C	-ABCD	-BE	ADE	$4Eff_C$
AC	-BCD	-ABE	DE	$4Eff_{AC}$
BC	-ACD	**-E**	ABDE	$-4Eff_E$
ABC	-CD	**-AE**	BDE	$-4Eff_{AE}$

Comparing the principal block arranged into the Yates order, with the aliasing matrix above, will indicate which effects are calculated from each row of the Yates table of analysis of the principal block.

The principal block containing the eight treatment combinations is derived from the total set by the normal method (TC'S with 0, 2, 4 .... letters in common with each of the defining contrasts see Table 3.8), by

definition, A, B, C, D and E will not appear, so the total set can be shortened, as seen in Table 3.14.

Table 3.14 Derivation Of Principal Block I

	Defining Contrasts		
Total Set	ABD	BCE	ACDE
(1)	**0**	**0**	**0**
~~AB~~	~~2~~	~~1~~	~~1~~
~~AC~~	~~1~~	~~1~~	~~2~~
~~BC~~	~~1~~	~~2~~	~~1~~
ABC	**2**	**2**	**2**
AD	**2**	**0**	**2**
~~BD~~	~~2~~	~~1~~	~~1~~
~~ABD~~	~~3~~	~~1~~	~~2~~
~~CD~~	~~1~~	~~1~~	~~2~~
~~ACD~~	~~2~~	~~1~~	~~2~~
BCD	**2**	**2**	**2**
~~ABCD~~	~~3~~	~~2~~	~~2~~
~~AE~~	~~1~~	~~1~~	~~2~~
~~BE~~	~~1~~	~~2~~	~~1~~
ABE	**2**	**2**	**2**
CE	**0**	**2**	**2**
~~ACE~~	~~1~~	~~2~~	~~3~~
~~BCE~~	~~1~~	~~3~~	~~2~~
~~ABCE~~	~~2~~	~~3~~	~~2~~
~~DE~~	~~1~~	~~1~~	~~2~~
~~ADE~~	~~2~~	~~1~~	~~3~~
BDE	**2**	**2**	**2**
~~ABDE~~	~~3~~	~~2~~	~~3~~
~~CDE~~	~~1~~	~~2~~	~~3~~
ACDE	**2**	**2**	**4**
~~BCDE~~	~~2~~	~~3~~	~~3~~
~~ABCDE~~	~~3~~	~~3~~	~~4~~

Therefore the eight treatment combinations (experiments) are :—

(1), abc, ad, bcd, abe, ce, bde, acde.

But they must be rearranged into the standard Yates order :—

(1), **a**d, **b**de, **ab**e, **c**e, **ac**de, **bc**d, **abc**.

The three other blocks of the 2^5 fractional factorial are given in Table 3.15.

Table 3.15 Three Remaining Blocks Of 2^5 Fractional Factorial

Block II Block I x a	**Block III** Block I x b	**Block IV** Block I x c
a	b	c
d	abd	acd
abde	de	bcde
be	ae	abce
ace	bce	e
cde	abcde	ade
abcd	cd	bd
bc	ac	ab

Table 3.16 Responses From Principal Block Of Fractional 2^5 Factorial

Treatment Combination	Response (Percentage Yield)
(1)	45.1
ad	60.2
bde	62.5
abe	46.8
ce	77.8
acde	49.8
bcd	53.6
abc	70.8

The results obtained from completing the principal block of the fractional factorial are shown in Table 3.16. The achieved yields, shown in Table 3.16 were a considerable improvement over previous yields, with the highest yield being 77.8%. It was obvious that there were some other significant factors included within the new experimental design that were responsible for the increase from a 42.5% yield. Table 3.17 lists the values of the effects, calculated from the Yates' analysis, enabling the significant variables and variable effects to be determined.

Table 3.17 Yates' Analysis Of Percentage Yield From Treatment Combinations Shown In Table 3.16 For Principal Block Of Fractional Factorial

Response	1	2	3	Effect
45.1	105.3	214.6	466.6 = Sum of Responses	—
60.2	109.3	252	$-11.4 = 4eff_a$	-2.85
62.5	127.6	-0.6	$0.8 = 4eff_b$	0.2
46.8	124.4	-10.8	$14.4 = 4eff_d$	3.6
77.8	15.1	4	$37.4 = 4eff_c$	9.53
49.8	-15.7	-3.2	$-10.2 = 4eff_{ac}$	-2.55
53.6	-28	-30.8	$-7.2 = 4eff_e$	-1.8
70.8	17.2	45.2	$76 = 4eff_{ae}$	19

Thus, Effect of Addition Temperature = -2.85

Effect of Methanol Addition Time = 0.2

Effect of Stirring Time = 3.6

Effect of Quantity of Methanol = 9.35 (aliased with - Methanol Addition Time and Stirring Temperature interaction)

Effect of Addition Temperature and Quantity of Methanol interaction = -2.55 (aliased with - Stirring Time and Stirring Temperature interaction)

Effect of Stirring Temperature = -1.8

Effect of Addition Temperature and Stirring Temperature interaction = 19 (aliased with Quantity of Methanol and Stirring Time interaction)

Figure 41 qualifies the identification of significant effects via a normal probability plot.

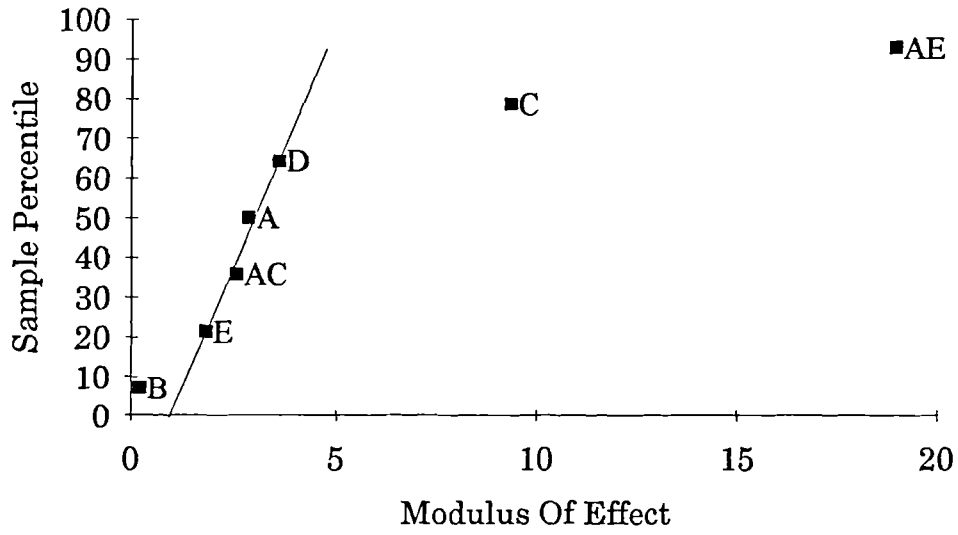


Figure 41 Normal Probability Plot Of Fractional Factorial Variable Effects

A reverse Yates calculation was carried out assuming E, AC, A, and D are not significant, the probability plot obtained is shown in Figure 42. It infers that aliases are an important factor as the assumed non significant effects, from the normal probability plot in Figure 41, do not lie on a straight line and some assumed significant effects do lie on the line.

Which aliases are important is impossible to ascertain, a significant effect can be cancelled by its significant alias and appear not to be significant. The fact that certain aliases are important should however be borne in mind.

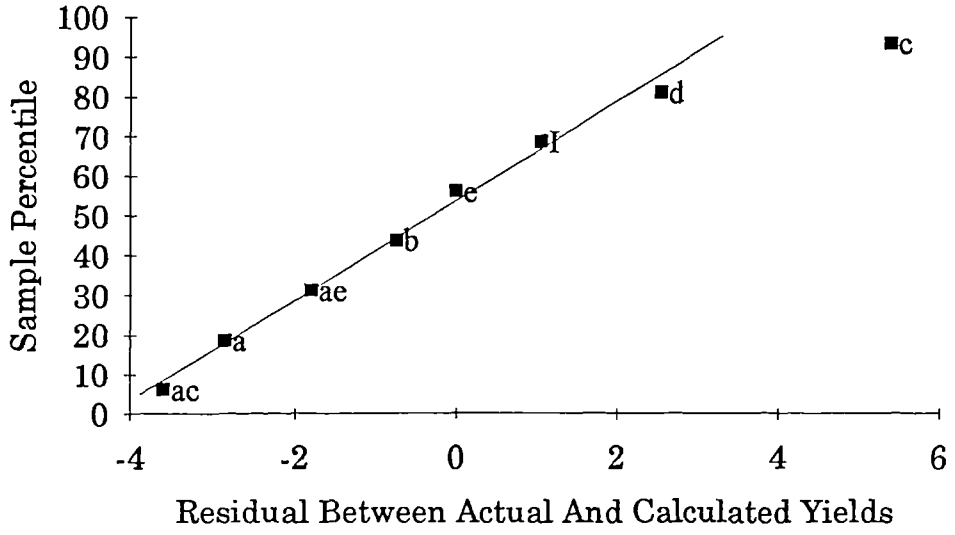


Figure 42 Reverse Yates Calculation Of Fractional Factorial

The most significant effect, from Table 3.17 and Figures 41 and 42, was the effect of addition temperature and stirring temperature interaction (aliased with quantity of methanol and stirring time interaction). This infers that increasing the addition temperature would increase its importance on the effect of the stirring temperature, which has a small negative effect. Conversely increasing the stirring temperature would increase its importance on the effect of the addition temperature, which also has a negative effect. Another significant effect was that of the quantity of methanol (aliased with - methanol addition time and stirring temperature interaction). This inferred that increasing the quantity of methanol would increase the yield, or decreasing the methanol addition time would decrease its effect on the effect of the

stirring temperature, which has a small negative effect, or vice versa. To help elucidate some of the confusion concerning the aliases a few probing experiments, taken from the three remaining blocks were performed. The probing experiments were conducted within the set levels of the chosen variables, avoiding needless complication. the results from these probing experiments are explained below.

Using the treatment combination notation, experiment 'bc' gave a yield of 62.4%, experiment 'abcd' gave a yield of 70.1%, experiment 'bd' gave a yield of 83.5% and experiment 'e' gave a yield of 90%. The first two experiments investigated the effect of changing the addition temperature at high and low stirring times at high quantities of methanol, high methanol addition times and no change in the stirring temperature (compare to 'bcd' : 53.6% and 'abc' : 70.8% from table 3.16), indicating that the higher yields were obtained with an addition temperature of 0°C, almost irrespective of the stirring times used . The third experiment, demonstrated the effect of changing the quantity of methanol at high and low addition temperatures at high stirring times, high methanol addition times and no change in the stirring temperature (compare to 'abcd' : 70.1% from Table 3.16), indicating that the better yield was obtained with a lower quantity of methanol and an addition temperature of -10°C. The fourth experiment demonstrated the effect of changing the quantity of methanol at high stirring temperatures, low addition temperatures, low methanol addition times and low stirring times. This obtained a high yield of 90% with a stirring time of half an hour. In a further experiment with the stirring time increased to one hour a yield of 95% was obtained. Replication of this final experiment produced yields in the region of 90%. Thus favourable conditions were, a rapid addition of a low quantity of methanol at a low temperature with subsequent stirring at a high temperature and for an intermediate length of time.

The final optimised procedure for synthesising 1–methoxy–3–methyl –2–phospholene oxide in 90% yield or better, was therefore as follows :—

To 400 mls of methylene chloride was added 25g (0.125 moles) of 1,1,1–trichloro–3–methyl–3–phospholene and the solution stirred at -10°C under a flowing atmosphere of nitrogen, whilst 136 mls (3 moles) of methanol was added over 15 minutes. The solution was then stirred at room temperature (25°C) for one hour before being neutralised with saturated sodium hydrogen carbonate solution. The organic layer was separated and the aqueous layer extracted with methylene chloride (5 x 100 mls). The organic layers were then recombined and the solvent removed on a rotary evaporator leaving a dark red orange oil,1–methoxy–3–methyl–2–phospholene oxide, in 90% yield or better.

Changing the solvent from methylene chloride to chloroform had no adverse effect on the yield. However the extraction process proved to be pH critical, requiring pH7 to maintain optimum extraction conditions.

Having optimised the second stage of the synthesis to levels similar to those for Stage I, a flow reactor could now be designed and constructed to facilitate larger scale production of 1–methoxy–3–methyl –2–phospholene oxide for subsequent full scale testing as a flame retardant in polyurethane foam systems.

Subsequently alternatives to methanol could be used in the reaction to synthesise large amounts of new phospholene oxides.

Table 3.18 Illustrates The Highest Yields Attained At Various Intervals Throughout The Multivariate Optimisation

Addition Temp.	Conc. Of 1,1,1–Trichloro –3–Methyl–3– Phospholene	Addition Time Of Methanol	Conc. Of Methanol	Stirring Time	Stirring Temp.	%age Yield
-15°C	50g in 400 mls	1 Hr	68 mls	2 Hrs	25°C*	24.8
0°C	50g in 400 mls	1 Hr	68 mls	2 Hrs	25°C*	42.5
0°C	25g in 400 mls	½ Hr	136 mls	2 Hrs	25°C*	57.0
-10°C	25g in 400 mls	¼ Hr	272 mls	½ Hr	25°C	77.8
-10°C	25g in 400 mls	½ Hr	136 mls	2 Hrs	-10°C	83.5
-10°C	25g in 400 mls	¼ Hr	136 mls	½ Hr	25°C	90
-10°C	25g in 400 mls	¼ Hr	136 mls	1 Hr	25°C	95

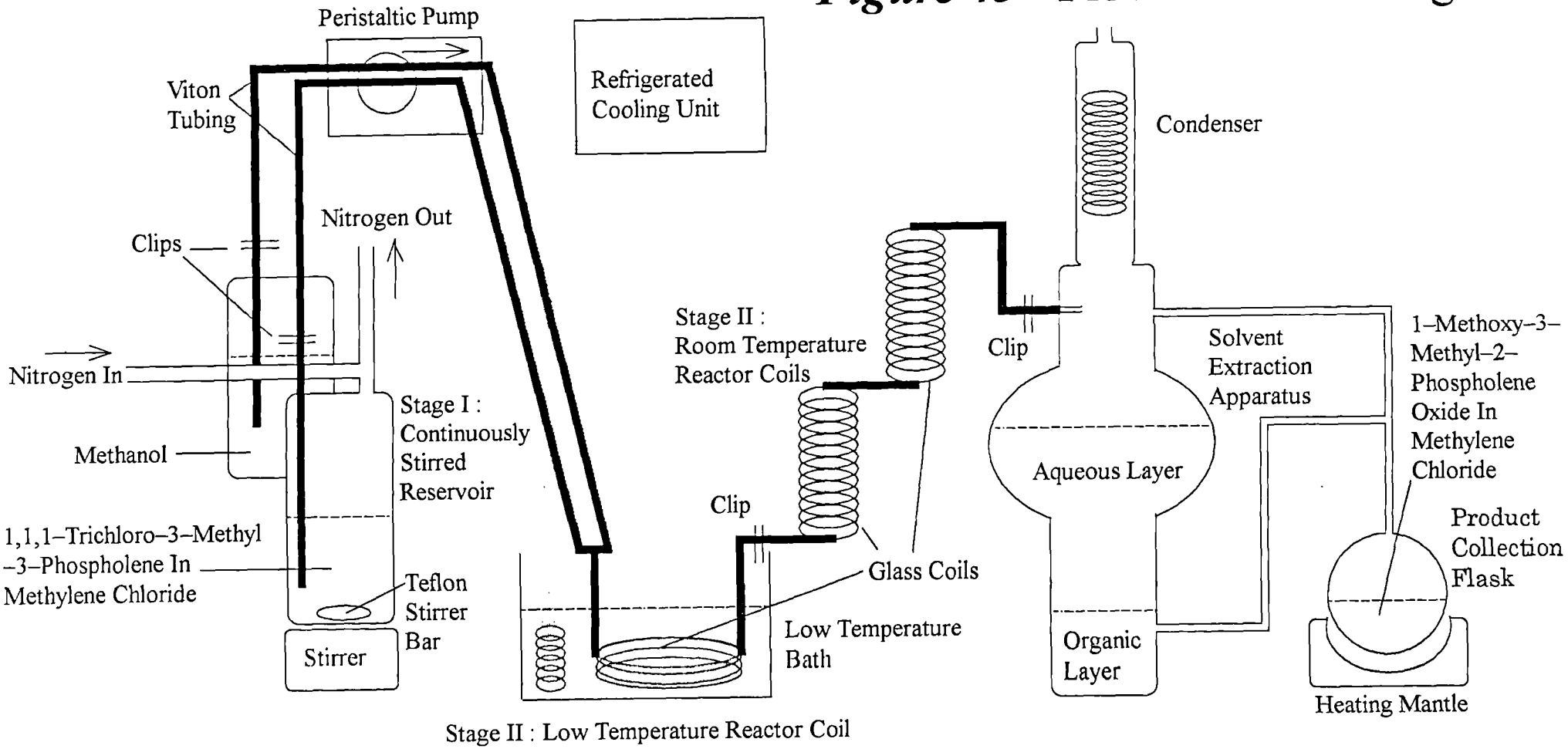
* Indicates solution stirred for 2 hours whilst reaching 25°C, i.e. not stirred for 2 hours at 25°C.

4.0 Design Of The Flow Reactor

As mentioned previously, the full scale testing of 1–methoxy–3–methyl–2 phospholene oxide (and subsequent derivatives), as a flame retardant in polyurethane foam systems at various loadings of flame retardant, would require between 0.5 and 1 kg of the oxide. The optimised Stage II batchwise synthesis described in section 3.2, resulted in about 15 grammes per experiment. Increasing the scale of this experiment in order to increase the amount produced, would require apparatus too large to use safely. Also, other parameters such as exothermicity of reaction, reaction interface, etc. would come into play when scaling up the reaction and the process may not be so efficient on a large scale. To facilitate the required large scale production, a flow reactor driven by a peristaltic pump was proposed, since then the so called 'plug' flow reactor functions as a continuous set of small scale experiments, i.e. at any one point in time only a small amount of reactants are reacting but the process is continuous. Initially it was intended to accomplish both Stage I and Stage II via a flow reactor system. However application of the Stage I synthesis to a flow reactor offered significant problems in both safety and design. The principle behind peristaltic pumping is that a length of tubing placed over the pumphead, termed the manifold tubing is squeezed by a roller, four times with each revolution of the pump head. This action draws the liquid through the tubing used. Despite the extreme corrosiveness of the phosphorus trichloride required in Stage I, combined with its high degree of air sensitivity, a suitable tubing was found for the peristaltic pump. The tubing in question being made of Viton — a copolymer of hexafluoropropene and vinylidene fluoride, with a life span in the peristaltic pump manifold of approximately 170 hours. However

after building a prototype flow reactor incorporating both Stage I and Stage II, a number of design flaws and possible "fail to danger" scenarios became evident upon commencement of preliminary testing of the set up. Namely, since the reaction time for the batchwise experiment Stage I was 20 hours, the flow reactor pumping rate had to be very slow to give the necessary lengthy dwell time in the glass reactor coils. Consequently the bore size of the manifold tubing had to be extremely narrow. Alternatively extremely long glass reactor coils could have been used, but since the internal diameter of the coils needed to be small, to give effective temperature distribution and turbid flow, then they would have been too difficult to construct. The slow pumping rate meant that during the preliminary testing it was very easy for a blockage to form in the reactor coils, despite isoprene being used in a 2:1 excess to minimise the build up of the solid product. This build up caused phosphorus trichloride to seep out of the tubing adapters, a major hazard! Even though the tubing was sufficiently impervious to attack by phosphorus trichloride, the points where the tubing was joined together or to the glass reactor coils was subject to seepage and consequently rapid deterioration. Also in order for the flow reactor to operate efficiently it was necessary to run it continuously for one week. If the flow reactor was operated only during the day there was a strong possibility of a solid build up of product on the tubing walls whilst the flow reactor was left dormant overnight, since there was no way of cleaning the system due to the hazardous reactivity of phosphorus trichloride. For overnight running, it would have to be monitored. Unmonitored running overnight was prohibited and dangerous and was therefore not feasible. To overcome these problems, it was decided to modify the flow reactor into a continuous stirred batch reservoir for the Stage I synthesis (the Stage I synthesis being accomplished via a

Figure 43 Flow Reactor Design



Stage II : Low Temperature Reactor Coil

batchwise process as before section 2.2.1) coupled to a peristaltically pumped flow reactor, in which Stage II of the synthesis is performed. The flow reactor system is shown in Figure 43. This meant that Stage I would be completed batchwise, synthesising approximately 0.5 kg of 1,1,1–trichloro–3–methyl –3–phospholene. This intermediate would then be dissolved in methylene chloride and put into a continuously stirred reservoir for use in the Stage II synthesis. The second stage could then be accomplished via a peristaltically pumped flow reactor with a low temperature reactor coil and room temperature reactor coils (as Stage II has a short reaction time), using the continuously stirred reservoir as a source of one reactant, 1,1,1–trichloro–3–methyl–3–phospholene in methylene chloride, as shown in Figure 43. The other reactant (an alcohol) was pumped directly out of a modified Winchester. A labelled photograph of the actual working flow reactor is shown in Plate 2 on the next page.

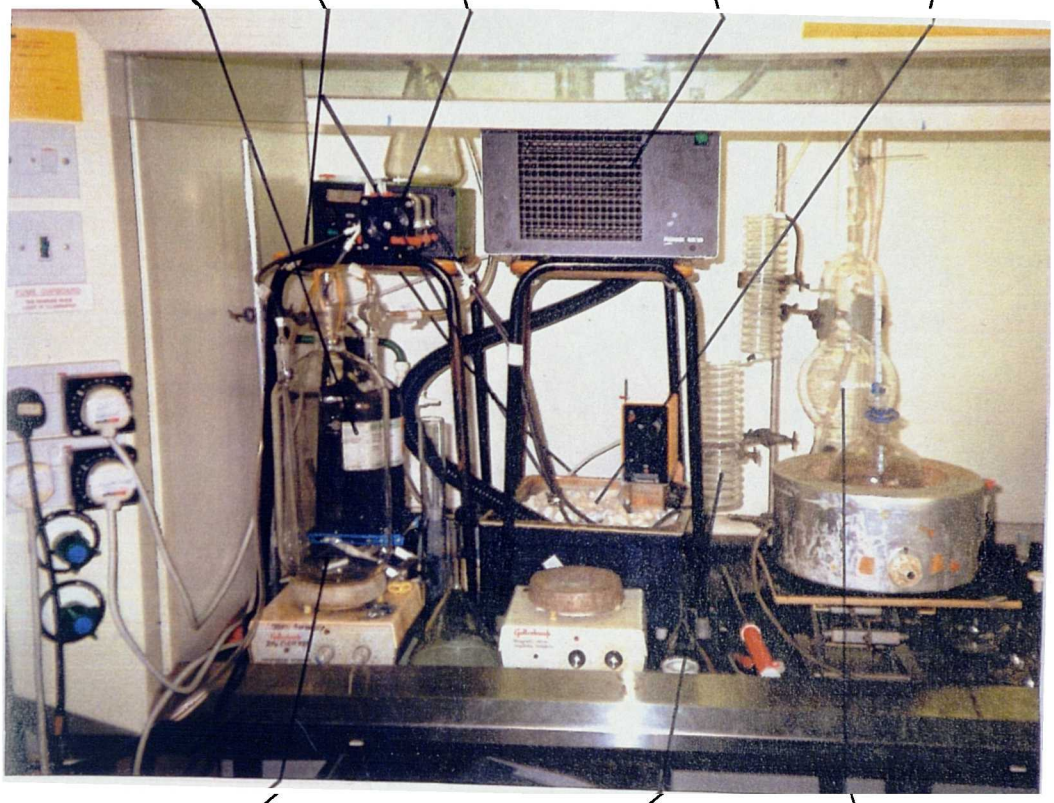


Plate 2 Photograph Of The Flow Reactor

This set up proved much more acceptable and meant that in 8 hours running time, 0.5 kg of the intermediate could be used up and the reactor safely shut down ready for the next day's operation.

4.1 Flow Reactor Operation

After a series of 'trial and error' runs on the flow reactor experimenting with the concentration of 1,1,1–trichloro–3–methyl–3–phospholene in methylene chloride and the pumping rate of the methanol, some final 'fine tuning' of the operating parameters (length of glass rector coils and glass reactor coil diameter and minimisation of bubbles of nitrogen forming in the reactor coils) a method of synthesising the novel target compound in high yield (> 70% conversion from starting reactants to end novel target compound), both efficiently and economically was formulated.

Approximately 0.5 kg of 1,1,1–trichloro–3–methyl–3–phospholene could be synthesised in one day using the optimised stage one batchwise process. The following day this intermediate could be added to 4 litres of methylene chloride under a flowing nitrogen atmosphere in the continuously stirred batch reservoir. If Stage II were to be attempted batchwise as before, 0.5 kg of the intermediate would have needed to be dissolved in 8 litres of methylene chloride. However since only a very small amount of the intermediate is reacting at any one time in the flow reactor, it was found that much less methylene chloride was required. For a batchwise experiment, the ratio of methanol to 1,1,1–trichloro–3–methyl–3–phospholene is 24:1 , with the flow reactor the ratio can be reduced to 12:1. This demonstrated the differences between flow systems and batchwise processes for certain reactions. The

0.5 kg of 1,1,1–trichloro–3–methyl–3 phospholene in 4 litres of methylene chloride was continually stirred in the reservoir tank held under a flowing nitrogen atmosphere. The peristaltic pump, a Watson–Marlow [Watson–Marlow, 1991] 100 rpm 503S with a 304MC micro cassette manifold pumphead, was set at eight revolutions per minute. By using a 2.54 mm bore Viton tube in the pump manifold the solution of 1,1,1–trichloro–3–methyl–3–phospholene in methylene chloride was pumped out at a rate of 3.44 ml min^{-1}. Methanol was pumped out of a modified Winchester (alcohol tank) at a rate of 1.6 ml min^{-1} by using a 1.65 mm bore viton tube in the pump manifold. The two piped reactants were mixed together via a 'Y' shaped connector just before entering the glass reactor coil held at a temperature of -10°C in the low temperature bath (the first part of the Stage II reaction). The combined pumping rate of 5.04 ml min^{-1} gave a dwell time of 15 minutes in the reactor coil. After these 15 minutes the reactants passed into a glass reactor coil held at room temperature, 25°C (the second part of the Stage II reaction). The length of these reactor coils was calculated to give a dwell time of one hour, before the reaction mixture entered the continuous solvent extraction apparatus. The solvent extraction apparatus was filled with 600mls of methylene chloride and about 5 litres of saturated sodium hydrogen carbonate solution, sufficient to neutralise the 0.5 kg of 1,1,1–trichloro–3 methyl–3–phospholene in methylene chloride in the reservoir tank. It was found that the extraction process was pH critical, neutral conditions being necessary for optimum extraction. The collection vessel was filled with 200 mls of methylene chloride and the heating mantle set at 50°C. The reactor was run for eight hours and then switched off. The pressure on the tubing in the pump manifold was relieved by removing them from the manifold. This was necessary to extend the life

span of the viton tubing and to prevent any overnight hazard. Clamping clips were used at specific points on the flow reactor set up, to prevent any of the reactants draining back into the reservoirs. The continuous solvent extraction apparatus was left running overnight to fully extract the product in the aqueous layer synthesised during the eight hour run. The flow reactor was operated only during the day (when it could be overseen) whilst the continuous solvent extraction apparatus could also be run overnight as it required no supervision. The subsequent day the solution of product was removed from the collection vessel and the solvent removed on a rotary evaporator (the solvent was recycled). Gas chromatography and spectroscopic analysis was carried out to show the purity of the product.

Using this flow reactor set up, an initial 800 grammes of 1–methoxy–3–methyl–2–phospholene oxide was synthesised. This was subsequently tested at the Albright & Wilson laboratory in Birmingham [Albright & Wilson] for its flame retardant properties in both flexible and rigid polyurethane foam formulations. The preliminary tests indicated that this novel compound had favourable fire retardant properties and therefore an additional 800 grammes was synthesised for further testing.

A further three additional derivatives were also synthesised using different alcohols in place of methanol. The second alcohol to be used was ethanol, anticipating the compound 1–ethoxy–3–methyl–2–phospholene oxide to be formed. The reaction conditions of the flow reactor were held at the same levels that were used when methanol was the alcohol. However the overall pumping rate and bore size of the viton tubing used to in the pump manifold for the alcohol were altered to maintain the same molar stoichiometry as before. The molar ratio in the two pumped channels between methanol (density 0.791 kg m^{-3}, MW = 32) and

1,1,1–trichloro–3–methyl–3–phospholene in methylene chloride was 12:1. To maintain this molar ratio for ethanol (density 0.801 kg m^{-3}, MW = 46) the bore size of the viton tubing used for pumping the ethanol was changed to 2.05 mm, to provide a pumping rate of 2.4 ml min^{-1}. This meant that the overall pumping rate had to be altered to give the same dwell times in the glass reactor coils, since with a pumping rate of eight revolutions per minute the volume of reactants had increased from 5.04 to 5.84 ml min^{-1}. The pumping rate was therefore reduced to seven revolutions per minute. The reason for maintaining this molar stoichiometry was that it could be used as a reaction reference for all syntheses involving alcohols. As yet there was no evidence to justify using a different molar stoichiometry, i.e. the process worked extremely well for methanol, so there was little point in changing it for subsequent alcohols. No attempts were made to optimise the production of 1–ethoxy–3–methyl–2–phospholene oxide, the flow reactor being approximately 65% efficient in its conversion of starting materials into end product.

With isopropanol (density 0.7820 kg m^{-3}, MW = 60), two Viton tubes of bore size 1.65 mm were used to give a pumping rate of 3.2 ml min^{-1} for the isopropanol and therefore the overall pumping rate was reduced to six revolutions per minute. Again no attempt to optimise the production of 1–isopropoxy–3–methyl–2–phospholene oxide was made, the flow reactor being approximately 55% efficient in its conversion of starting materials into end product.

The last alcohol used in the flow reactor was tertiary butanol (density 0.786 kg m^{-3}, MW = 74), however this is a crystalline solid (m.pt. 26°C) at room temperature and so a suitable solvent was required. The solvent recommended in the handbook of Chemistry and Physics 71st

edition was diethyl ether, however this solvent had disastrously damaging effects upon the tubing used in the peristaltic pump. A search for an alternative solvent showed methylene chloride to be the most acceptable and this solvent was already being used for the intermediate reactant 1,1,1–trichloro–3–methyl–3–phospholene in Stage II. Therefore 2 kg of tertiary butanol was dissolved in 600 mls of methylene chloride, the bore size of viton tubing used for pumping the tertiary butanol was 2.05 mm and the overall pumping rate was being set at seven revolutions per minute. Problems also occurred in the low temperature reactor coil, as the solid tertiary butanol was liable to crystallise out of solution on to the walls of the reactor coil building up into a blockage, which if left caused severe problems. Additional methylene chloride was periodically pumped into the reactor coil to rectify this narrowing and possibility of blockages. The overall conversion rate on the flow reactor for the production of 1–tertbutoxy–3–methyl–2–phospholene oxide was 35%. Steric hindrance from the tertiary butyl group was thought to be primarily responsible for this poor yield and so no attempts at optimisation were tried.

In hindsight the peristaltic pumping method proved inadequate and hazardous. The only non–perishable tubing available was the extremely expensive black Viton tubing. Even this inert copolymer of hexafluoropropene and vinylidene fluoride was susceptible to chemical attack by 1,1,1–trichloro–3–methyl–3–phospholene resulting in its gradual depolymerisation and therefore additional physical deformation in the pump manifold, after approximately 25–30 hours pumping at the required rate, the Viton tubing expanded and from then on it was extremely susceptible to splitting, thus becoming a major hazard. A cheaper and less hazardous system of moving the reactants through the reactor would be to use an inert gas, e.g. nitrogen as the propulsion

mechanism with the flow rate being accurately monitored and adjustable. Glass tubes, impervious to chemical attack, could then be used throughout the reactor. This would have the additional advantage of providing a visible means of monitoring the condition of the flow reactor as well.

In all, in excess of 1 kg of each of the four phospholene oxides, 1 methoxy 3 methyl–2–phospholene oxide, 1–ethoxy–3–methyl–2–phospholene oxide, 1–isopropoxy–3–methyl 2 phospholene oxide and 1 tertbutoxy–3–methyl–2 phospholene oxide were synthesised on the flow reactor. These compounds were then rigorously tested, for their flame retardant behaviour, in various rigid and flexible foam formulations. The flammability tests to be performed were the standard DIN 4102 surface and edge exposure tests, the rigorous Epiradeateur or NF P92–501 test and limiting oxygen index studies.

5.0 Introduction To Polyurethane Chemistry

Polyurethanes are all around us playing a vital role in many industries, from ship building to footwear; construction to cars, all since Otto Bayer and co–workers realised the commercial potential of urethanes in 1940. Their variety and diversity of forms is continuously increasing. Rigid polyurethane foam is an effective practical thermal insulation material. Flexible foams are comfortable, durable and aesthetically pleasing which has led to their extensive use in vehicles, homes and places of work [Woods, G. 1990].

All polyurethanes are based on the exothermic reaction of polyisocyanates with polyol molecules, containing hydroxyl groups (see Figure 44). No unwanted by–products are given off and because the raw materials react completely, no "after cure" treatment is necessary. Relatively few basic isocyanates and a range of polyols of different molecular weights and functionalities are used to produce the whole spectrum of polyurethane materials, from low density foams to solid polyurethanes, very soft elastomers to rigid plastics. Foaming occurs when a small amount of water is added during polymerisation. Water adds to the isocyanate groups giving carbamic acids which spontaneously lose carbon dioxide (see Figure 45). Both the reaction between the isocyanate and polyol and isocyanate and water generate heat. If the carbon dioxide produced from the water—isocyanate reaction is used to blow the foam the lowest density that can be achieved in practice for flexible foams is in the region of 20–22 kg m^{-3}. Below this density methylene chloride or trichlorofluoromethane (CFM–11), vaporised by the heat of reaction, must be used to provide auxiliary blowing and cooling.

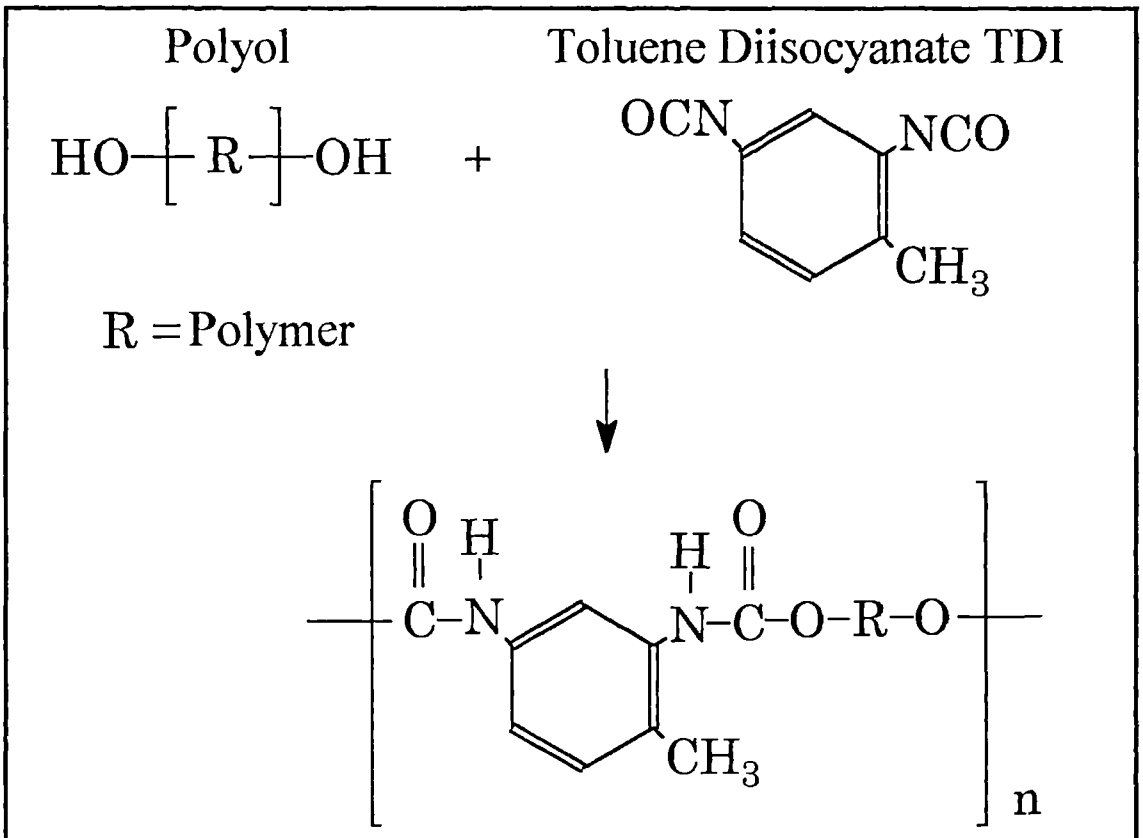


Figure 44 The Polyurethane Addition Reaction

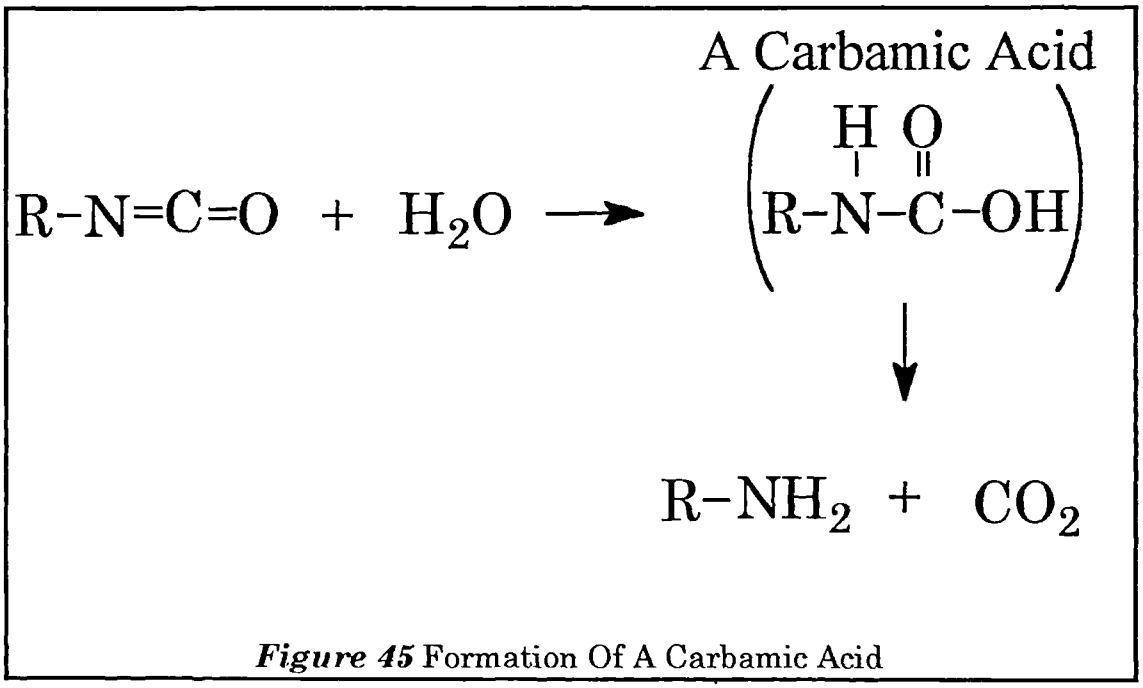


Figure 45 Formation Of A Carbamic Acid

5.1.1 The Chemicals

Most isocyanates and polyols used in the manufacture of polyurethanes are liquid at ambient temperatures and are easily handled, although all isocyanates are extremely toxic. The reactions which produce the solid polymer are rapid and normally complete within two minutes. The solid foam product can normally be handled within five minutes from the start of mixing, although it is safer to allow the foams to stand overnight (referred to as "curing"), whilst any unreacted isocyanate evaporates or combines with atmospheric moisture.

5.1.2 Isocyanates

The properties of the final polyurethane may be modified by varying the type of isocyanate. Several aromatic and aliphatic isocyanates are available, but about 95% of all polyurethanes are based on two of them. These are toluene diisocyanate (TDI), and diisocyanato–diphenylmethane (MDI) and its derivatives. Both materials are mixtures of isomers, 2,4 and 2,6 isomers for TDI in an 80:20 mix, and the 2,4' and 4,4' isomers for MDI which usually contains only a small amount of the 2,4' isomer (see Figure 46). TDI is used mainly in the production of low density foams, development of MDI was necessary as the volatility of TDI caused severe problems when TDI based rigid foams were sprayed in enclosed spaces. MDI is used primarily for the production of rigid foams. The sales of MDI overtook those of TDI in 1984, and rigid foams now occupy approximately 70% of the market share of polyurethane foams.

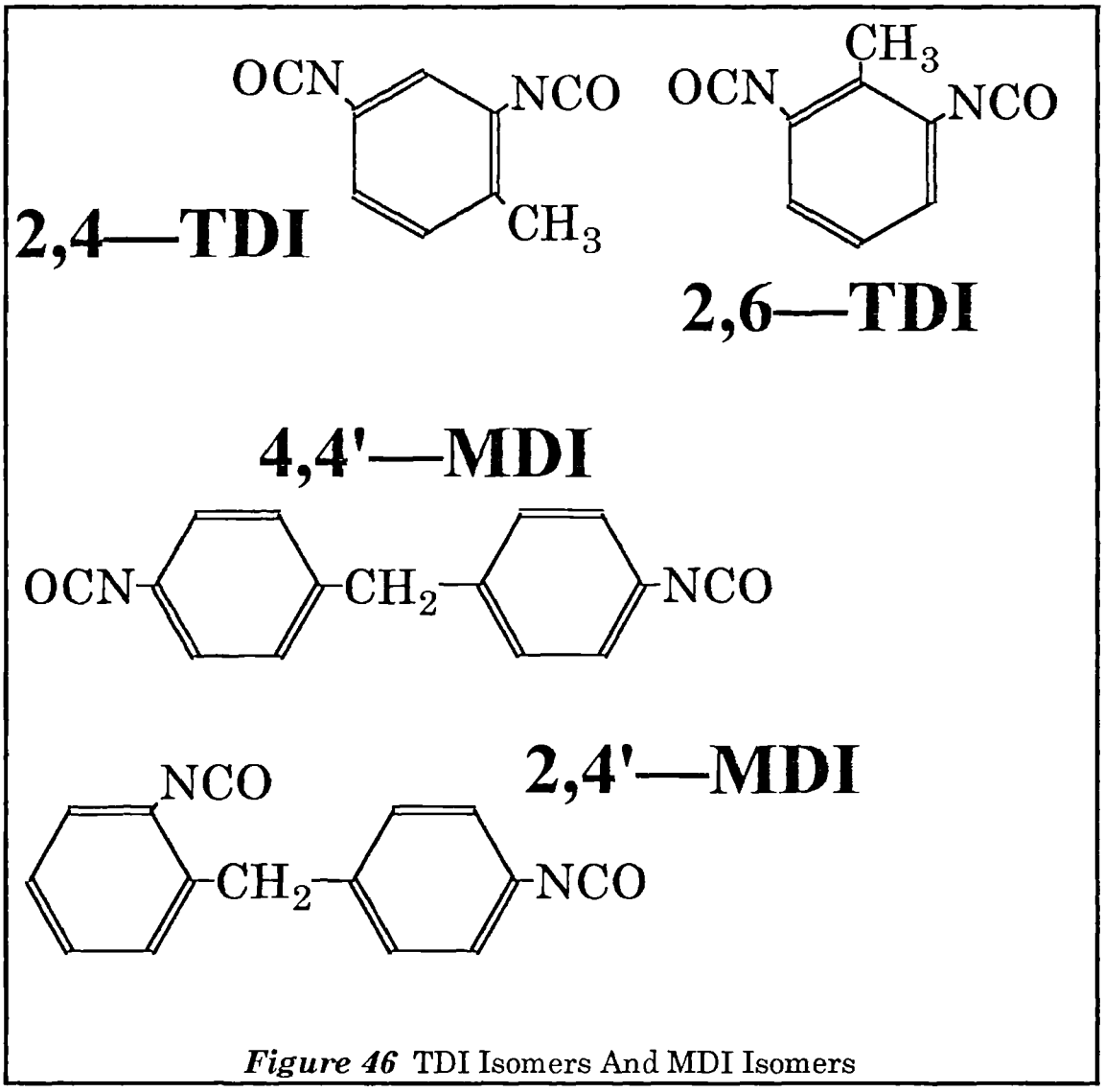


Figure 46 TDI Isomers And MDI Isomers

5.1.3 Polyols

Some 90% of the polyols used in the manufacture of polyurethanes are polyethers with terminal hydroxyl groups. Hydroxyl terminated polyesters are used to obtain polyurethanes with special properties. The choice of polyol, especially the size and flexibility of its molecular structure and its functionality (the number of isocyanate–reactive hydroxyl groups per molecule of polyol) controls, to a large extent, the degree of cross linking achieved in the foam produced. To obtain a rigid foam there must be a stiff polymer network and hence a high degree of

cross linking; for flexible foams a proportionally lesser degree of cross linking is needed.

5.1.4 Additives

In addition to isocyanates and polyols, a wide range of auxiliary chemicals may be added to control and modify both the polyurethane reaction and the properties of the final polymer. All practical polyurethane systems include at least some of these auxiliary chemicals.

5.1.4.1 Catalysts

Tertiary amines and organometallic compounds are used as catalysts to speed up the reaction of the isocyanate with the polyol. These include aliphatic and aromatic tertiary amines (see Figure 47), and organometallic compounds, especially tin compounds, although compounds of lead are also used. Alkali metal salts of carboxylic acids and phenols, and symmetrical triazine derivatives are used to promote the polymerisation of isocyanates. The mechanism of catalysis by a tertiary

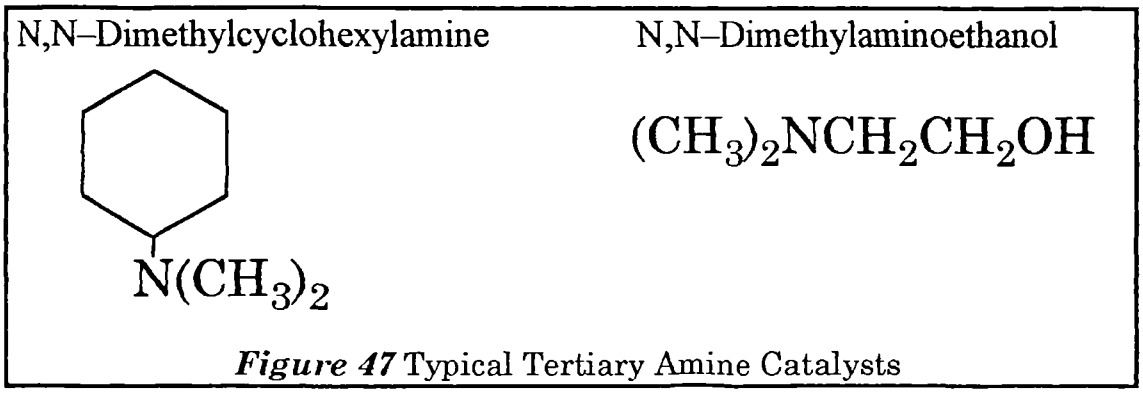


Figure 47 Typical Tertiary Amine Catalysts

amine involves the donation of electrons by the tertiary nitrogen to the carbonyl carbon of the isocyanate group thus forming a complex

intermediate. The catalytic activity of a tertiary amine depends on its structure and basicity, increasing with increasing basicity but reduced by steric hindrance of the aminic nitrogen. Organometallic catalysts (typically stannous octoate) are used to accelerate the urethane polymerisation reaction by forming an intermediate complex with an isocyanate group and a hydroxyl group of the polyol.

5.1.4.2 Chain Extenders And Cross Linking Agents

Chain extenders are used in the manufacture of flexible foams, where the chain extender reacts with diisocyanate to form a polyurethane or polyurea segment in the urethane polymer. Cross linking agents are used to increase the covalent bonding in rigid foam systems. These are low molecular weight polyols or polyamines. Chain extenders are difunctional substances, glycols (e.g. ethylene glycol), diamines (e.g. m-phenylene diamine) or hydroxy amines (e.g. diethanolamine); cross linking agents have functionality of three or more (e.g. triethanolamine).

5.1.4.3 Blowing Agents

Cellular polyurethanes are manufactured by using blowing agents to form gas bubbles in the polymerising mixture. Flexible polyurethane foams are usually made using the carbon dioxide formed in the reaction of water and diisocyanate either as the sole blowing agent or as the principal blowing agent in association with either trichlorofluoromethane (CFM–11) or methylene chloride, or a combination of both. The usual blowing agent for rigid foams is CFM–11. The low thermal conductivity of the CFM–11 vapour which is retained in the closed cell rigid foam is important in giving a cellular product with highly effective insulating properties. As

already mentioned the use of CFC's constitutes an environmental problem. Alternatives under investigation are hydrochlorofluoroalkanes (HFA 123, HFA 141b and HFA–22) and pentane, both produce very inferior foams with poorer physical properties and pentane blown foams constitute an additional increased flammability hazard.

5.1.4.4 Surfactants

Surface active materials are essential ingredients in the manufacture of most polyurethanes, helping to mix incompatible components of the reaction mixture. They are particularly useful in controlling the size of the foam cells by stabilising the gas bubbles formed during nucleation and may stabilise the rising foam by reducing stress concentrations in the thinning cell walls. Most flexible and rigid foams are made using organosiloxanes or silicone based surfactants. Silicone surfactants for rigid foams have a greater surface activity than those for flexible foams. A typical surfactant is a polydimethylsiloxane–polyether graft copolymer surfactant, the surfactant structure may be modified by changing the length of the polydimethylsiloxane backbone and the number of the pendent polyether chains.

5.1.4.5 Colouring Materials

Most low density flexible foam is colour coded during manufacture to identify the grade and the density of the foam. Rigid foams, being mostly brown coloured from the polymeric MDI used, and sold enclosed within opaque covering materials are often made without added colourants. The usual method of colouring is by the addition of organic and inorganic pigment pastes to the foam reaction mixture.

5.1.4.6 Fillers

Particulate and fibrous fillers may each be used in most kinds of polyurethanes. Particulate fillers are used in flexible polyurethane foams to reduce their flammability and, particularly in the USA, to increase their resistance to compression (e.g. clays and calcium carbonate). Fibrous fillers give increased stiffness and therefore increase the operating temperature of rigid foams (e.g. milled glass fibres).

5.1.4.7 Flame Retardants

Following the reduction of CFC usage, together with a demand for higher quality upholstery, the average density of flexible slabstock foams is increasing. Coupled with this, is the requirement that foams manufactured need to meet tougher flammability regulations, particularly in the USA and the UK. In the UK, the implementation of the Furniture and Furnishings Fire Safety Regulations in 1988, has prohibited the sale of domestic furniture, beds, mattresses, cushions and pillows containing any flexible polyurethane foams that are not combustion modified.

Low density, open cell foams having a large surface area and a high degree of air permeability present a considerable burning hazard. Deaths from fires, in which foams were the major cause for concern, are never far from the news headlines.

The choice of flame retardant system in any specific circumstance will depend upon the service application of the polyurethane foam, the assessment of the fire hazard and any legal requirements. A typical combustion modified high resilience foam includes either a melamine or intumescent graphite, which, on exposure to a flame forms a heat

resistant char. The testing of uncovered foams is of limited value, as most flexible and rigid foams are rarely used alone. However it does yield vital information on the inherent flammability of the particular foam. Foams are usually enclosed within a composite article such as an upholstered chair or a refrigerator where the covering material is the most important factor determining ignitability and the primary fire hazard. Both the ignitability and the burning rate of polyurethanes may be reduced by the addition of flame retardants which operate through one or more of the following mechanisms :—

- Provision of a heat sink by filling with incombustible materials to delay ignition and reduce the rate of burning.
- Provision of an energy sink and means of diluting the combustible gases by filling with substances that decompose on heating to give incombustible products such as water and carbon dioxide.
- Modification of the burning mechanism by filling with materials, such as halogenated flame retardants, which when heated produce species which inhibit the combustion process.
- Inducing char formation by the use of additives.

The most widely used flame retardants in both flexible and rigid foam systems are chlorinated phosphate esters, incorporation of 5—10% chlorinated phosphate esters meets many ignitability standards for furniture and automotive seating. They have a significant effect upon the ignitability of foams by a small heat source and they can show marked reductions in the rate of burning in small scale tests without adversely effecting the foam system and properties of the product.

The addition of alumina trihydrate gives a further reduction in flammability and minimises the increase in smoke formation on burning,

as a consequence of the addition of halogenated organic phosphates. Melamine is also used together with phosphate flame retardants in flexible foams for furniture cushions, it gives good resistance to smouldering combustion. Broadly speaking the flame retardants used can be categorised into three different classes (see Table 5.1) : —

- Non–reactive liquid flame retardants.
- Compounds that react with isocyanates to become bound into the polymer network.
- Some other materials (fillers) that reduce the rate of burning.

They function in one or more of four general modes :—

- By cooling in the solid phase, the physical bulk of materials such as melamine and alumina trihydrate added to a polyurethane foam act as a heat sinks.
- By formation of a protective layer of char in the condensed or liquid phase, this is the mode of action found with phosphorus compounds.
- Being mixed in the solid and vapour or gaseous phases, as is the case with melamine and effectively behaving as dilutents.
- By interference with the radical combustion mechanisms in the vapour or gas phase, which is the fundamental mode of action of halogens.

As described earlier, phosphorus containing flame retardants are very effective in materials with a high oxygen content such as polyurethanes, polyester resins and cellulosics, where the char layer, formed through dehydration (see Figure 48), is very effective at resisting

high temperatures and protects the underlying polymer from attack by oxygen and heat.

Table 5.1 Examples Of Flame Retardants Used In Polyurethane Foams

Additive	*Typical Application*
A. Non–Reactive Liquids	
Tris(2-chloropropyl) phosphate	All polyurethane foam systems
Tris(2-chloroethyl) phosphate	Polyether based foam systems
Tris(2,3-dichloropropyl) phosphate	Polyether based foam systems
Dimethyl methyl phosphonate	Rigid foam systems
B. Reactive Additives	
Tris(polyoxyalkyleneglycol) phosphonate esters	Flexible and semi–rigid foam systems
Tris(halogenated polyol) phosphonates	Flexible and rigid foam systems
C. Fillers	
Ammonium salts, sulphate, polyphosphate etc.	Together with halogenated additives in rigid foam systems
Alumina trihydrate	All polyurethane foam systems
Melamine	All polyurethane foam systems
Calcium carbonate	Heat absorbing filler

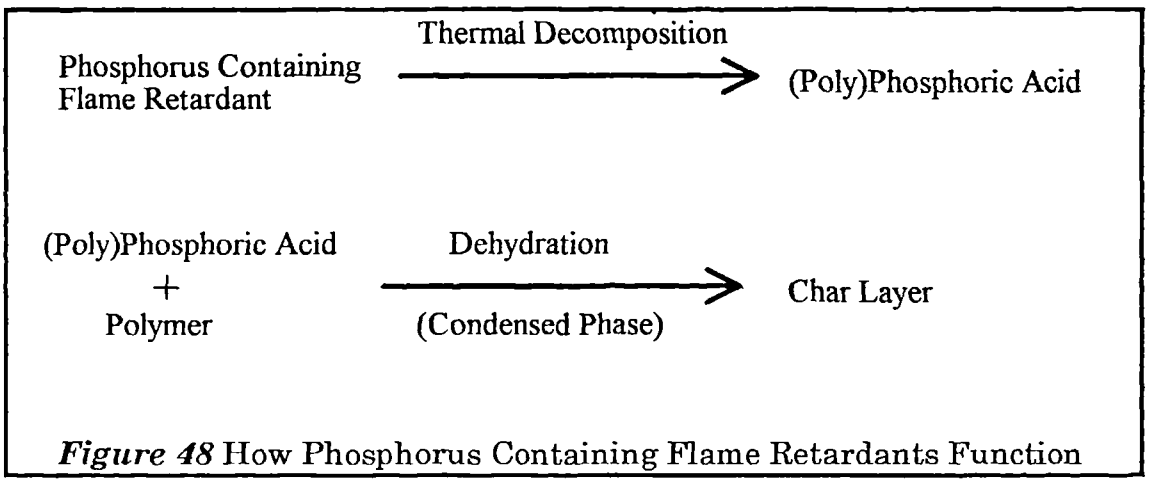


Figure 48 How Phosphorus Containing Flame Retardants Function

The effectiveness of halogen containing flame retardants increases in the order :— F < Cl < Br < I

In practice fluorine and iodine are not used. Brominated flame retardants are quite popular for polyurethane applications. However, because a significant proportion are based on polybrominated diphenyl ethers, which can give rise to dioxins on combustion, their use is frowned upon. The exclusion of chlorine because of its harmful effects upon the environment will almost certainly follow. However, as noted previously, halogenated flame retardants operate in the vapour phase in three stages.

I. Flame retardant breaks down to give halogen radicals

$$RX \rightarrow R\cdot + X\cdot$$

II. Halogen radical reacts to form a hydrogen halide

$$X\cdot + RH \rightarrow R\cdot + XH$$

III. The hydrogen halide interferes with the radical chain mechanism of combustion :—

$$HX + H\cdot \rightarrow H_2 + X\cdot$$

$$HX + OH\cdot \rightarrow H_2O + X\cdot$$

High Energy Low Energy

The choice of flame retardant for foam applications is also influenced by the properties of the flame retardant and its effect on the properties of the subsequent foam produced. Typical properties effected are : —

- Ageing properties of foam.
- Dimensional stability of foam.
- Effectiveness of flame retardant.

- Fogging.
- Scorch.
- Volatility.
- Molecular weight.
- Chemical stability.

Ageing properties of foams can be adversely affected by a flame retardant and are important for all polyurethane foams.

The dimensional stability of a foam is an important factor for rigid foams and is concerned with preventing shrinkage and distortion throughout the foam specimen.

The effectiveness of a flame retardant in a polyurethane foam towards the ignitability and burning rate of the foam is of obvious importance.

The expression fogging refers to the semi–opaque or translucent film that periodically builds up on the inside of vehicle windscreens. It is caused by deposits of volatile material given off by the interior components (e.g. the foam in the seating) when subject to high temperatures such as result from exposure to direct sunlight. The addition of some flame retardants to polyurethane foams used in automotive applications tends to worsen windscreen fogging.

Scorch is the term used to describe the yellow/brown discoloration occasionally observed in the centre of large slabstock foam blocks. The discoloration is caused by the (thermo) oxidative breakdown of the foam at high temperatures and can be enhanced by the presence of a flame retardant.

The volatility of a flame retardant affects its applications, volatile flame retardants are used in rigid foams only, being retained within the

closed cell structure. Flexible foams require less volatile flame retardants to prevent their loss through evaporation.

The molecular weight affects the application of a flame retardant, being comparable to its volatility. Hence high molecular weight flame retardants are used in flexible foam formulations.

The chemical stability of the flame retardant is important where the product is stored in contact with other compounds in the foam formulations, in particular amine catalysts. In flexible polyester foams, flame retardants must have good hydrolytic stability to prevent acidic species being formed, which cause cleavage of the ester groups.

5.1.5 Types Of Polyurethane Foams

The molecular weight and chemical composition of the isocyanate and polyol have a significant influence on determining both the physical properties and burning behaviour of a given polyurethane foam. There are two standard types, flexible and rigid. Flexible foams are almost exclusively derived from TDI whereas rigid foams utilise derivatives of MDI, as described earlier.

5.1.5.1 Flexible Polyurethane Foams

There are currently three routes available for the manufacture of flexible polyurethane foams, polyester, polyether and (combustion modified) high resilience foams. Hot and cold moulded flexible foams are derived from polyether foam polyols and high resilience foam polyols respectively.

5.1.5.1.1 Polyester Foams

Polyester foams are based on polyols or 'resins' manufactured from adipic acid and ethylene glycol. The foams produced from such polyols possess excellent tensile strength and elongation properties and are significantly stiffer than their polyether or high resilience foam counter parts. Polyester foams have a unique property in that when they are briefly exposed to a flame, their surface becomes extremely tacky. When slit into thin sheets this property of the foam provides a cost effective means of bonding textiles together by a process which is commonly referred to as flame lamination. The principle application of this technology lies in the manufacture of vehicle seat covers and head liners.

The relatively high thermal stability of polyester foams reduces their dependence on high loadings of flame retardants to achieve certain flammability standards. However as esters are readily hydrolysed under acidic conditions, any potential flame retardant must possess a high degree of chemical stability.

A typical 30 kg m^{-3} polyester foam would consist of the following ingredients as shown in Table 5.2.

Table 5.2 Typical Flexible Foam Formulation Based On A Polyester Polyol

Component	Composition/parts by weight	
Polyester Polyol	100	
Water	4	
N–ethylmorpholine	1	Amine Catalyst
N–cetyldimethylamine	0.3	Amine Catalyst
Silicone Surfactant	1	
Stannous Octoate (10% solution)	0.2	Catalyst
Toluene Diisocyanate (TDI)	50.8	
Flame Retardant	10—20	

The polyester polyols used have a molecular weight of around 2500, the amount of isocyanate used is calculated to give a slight excess over and above that required to fully react with the water and polyol components. The additional isocyanate is used to control the hardness of the foam and optimise tensile, elongation and recovery properties.

5.1.5.1.2 Polyether Foams

Polyether foams are based on polyols derived from reacting propylene and ethylene oxides with, for example, glycerol. Polyether polyols provide some of the most diverse ranges of foams with densities ranging from in excess of 40 kg m^{-3} to less than 10 kg m^{-3}, although the latter are only obtainable using auxiliary blowing agents. Polyether foams are more resilient than polyester foams, making them ideally suited for

furniture and bedding applications. Foams derived from polyether polyols possess a high proportion of saturated carbon atoms which when combined with the type of porous structures presented by cellular plastics, provides a material of very low ignition resistance. These foams are the most difficult to effectively flame retard, being prone to smouldering and large variations in flammability performance, when manufactured with high air porosities.

An example of the typical 30 kg m^{-3} density furniture foam formulation is shown in Table 5.3.

Table 5.3 Typical Flexible Foam Formulation Based On A Polyether Polyol

Component	Composition/parts by weight	
Polyether Polyol	100	
Water	3.4	
Air Products DABCO 33LV	0.15	Amine Catalyst
Union Carbide NIAX A1	0.05	Amine Catalyst
Silicone Surfactant	1	
Stannous Octoate (100% solution)	0.27	Catalyst
Toluene Diisocyanate (TDI)	44.3	
Flame Retardant	10—20	

The polyols used for flexible polyether foams have a molecular weight of 3500, as with polyester foams, there is also a slight excess of isocyanate. Note that the stannous octoate catalyst is used in its undiluted form.

5.1.5.1.3 High Resilience Foams

The original concept behind the manufacture of high resilience foam was the production of a material which more closely approached the handle and feel of latex foams. By far the most popular route for producing high resilience foams at present relies on the use of modified polyether polyols containing polymer dispersions which are capable of being foamed with standard toluene diisocyanate. Three such polyols currently dominate both the standard and combustion modified high resilience foam market, Poly Harnstoff Dispersion (PHD) polyols, Poly Isocyanate Poly Addition (PIPA) polyols, but by far the most popular are polymer or copolymer polyols. This last type of polyol is produced by the in situ polymerisation of styrene and acrylonitrile in a polyether polyol. The polymer polyols used for standard high resilience foam production have a polymer dispersion content of around 10%. Those used for combustion modified foams may have polymer contents as low as 5%. High resilience foam formulations are identical to those for polyether foams except that the polyol is a polymer polyol as described and not a simple polyether polyol.

High resilience foams tend to melt or shrink when exposed to a flame and have long been recognised as having superior ignition resistance compared to standard polyether foams. In order to improve their flammability resistance still further, a technique has been devised of incorporating solid melamine powder into these foams during their initial stages of manufacture. When combined with a liquid phosphorus containing flame retardant, the melting action of the foam produces a high concentration of decomposing melamine at the flame front. The phosphorus in the flame retardant ensures the build up of a char layer during combustion which slows down and eventually extinguishes the

burning foam. This mechanism of altering the rate at which high resilience foams burn has been popularised by the expression Combustion Modification.

5.1.5.1.4 Hot And Cold Moulded Flexible Foams

Hot and cold moulding are processes which are almost universally employed for the production of vehicle seating foams. Hot moulding refers to a process by which a polyether foam polyol, blowing agent, catalyst, surfactant and isocyanate are blended together and injected into a heated (ca 40°C) metal mould shaped to the design of the required seat component. Toluene diisocyanate is always used in the manufacture of hot moulded foam requiring the finished component to be held at an elevated temperature (150°C) to ensure satisfactory curing.

Cold moulding relies on the use of high resilience polyols in combination with MDI and TDI to produce the foamed article. The superior curing characteristics of foams based on MDI are such that no post treatment at elevated temperatures is required. The choice of hot or cold moulding for producing a particular foamed part depends on the physical properties demanded by the manufacturer. Foams derived from TDI can be produced with lower densities and higher hardnesses but are generally more flammable in comparison to MDI based cold mould foams.

5.1.5.2 Rigid Polyurethane Foams

These are manufactured using polymeric isocyanates derived from MDI. Whereas the polyols available for flexible foams are manufactured over a comparatively narrow band of molecular weights, rigid foams have a far greater diversity of raw materials.

Rigid foam polyols may be derived from sorbitol, sucrose, pentaerythritol, toluene diamine, phenols, etc. and may include polyester and polyether components. The different chemical composition of each polyol can greatly affect both the processing characteristics and the burning behaviour of a particular rigid foam system. Practically all rigid foam systems rely on the use of chlorinated fluorocarbon blowing agents (CFC's) for their manufacture. Environmental concerns have prompted moves towards reducing the consumption of these compounds in favour of increased water blowing or the use of hydrocarbons (pentane) or hydrochlorofluoroalkanes (HFA's). All the alternative blowing technologies are deleterious to the physical properties and flammability performance of the finished foam.

A typical rigid form formulation based on an aromatic amine initiated polyol (blend of 75% propoxylated Mannich adduct and 25% propoxylated alkanol amine) is shown in Table 5.4.

Table 5.4 Typical Rigid Foam Formulation Based On An Aromatic Amine Initiated Polyol

Component	Composition/parts by weight	
ARCO ARCOL 3758	100	Polyol
Water	0.5	
Dimethyl Cyclohexylamine	1.5	Amine Catalyst
Air Products DABCO DC193	1	Surfactant
Arcton 11 : Trichlorofluoromethane	35	Auxiliary Blowing Agent
Stannous Octoate (10% solution)	0.2	Catalyst
Diisocyanato–Diphenylmethane	182.5	MDI
Flame Retardant	10—20	

5.1.5.2.1 Rigid Composites Or Laminates

These foams are traditionally based on polyether polyols derived from sucrose/amine combinations or aromatic amines in the case of high speed lamination applications.

As a result of their lower hydrogen saturation, foams produced from aromatic amines are far less flammable than those produced from aliphatic sucrose amines, and often require lower loadings of flame retardant to achieve acceptable standards of flame retardancy.

Whilst polyether polyols form by far the largest proportion of raw materials used for rigid foam lamination, there is a steady growth in the use of aromatic polyester polyols. These are usually based on either phthallic anhydride or dimethylterphthalate. Such polyols can only be processed effectively using a higher stoichiometric excess of isocyanate. The excess of isocyanate is trimerised using special catalysts to produce what is commonly referred to as a polyisocyanurate or PIR foam.

One of the characteristics of foams based on aromatic polyester polyols is their excellent flame retardancy, often achieving a B2 standard with the German DIN 4102 test without the addition of a flame retardant. This technology is well established in the USA where foams are required to pass the ASTM E84 tunnel test., an intermediate scale surface spread of flame test. One of the drawbacks of producing foams with large excesses of MDI, is a tendency of the surface of the foam to become very friable or powdery. This problem is exacerbated in systems where attempts have been made to replace CFC's by increased water blowing.

Some of the shortcomings of polyester polyols may be overcome by blending with polyether polyols. This is a particularly useful, and cost effective method of producing flame retarded foams due to the inherently lower flammability of the polyester component.

5.1.5.2.2 Two Component Foams

A significant proportion of the foams used in rigid applications are derived from pre–packaged blends of chemicals referred to as two component (foam) systems. The A component is usually a standard grade of polymeric MDI whilst the B component comprises a formulated polyol system incorporating catalysts, surfactant, blowing agent and flame retardant. Typical uses of two component foam systems include discontinuous lamination, pour in place and pipe insulation. Some flexible moulded foams are also sold as preformulated two component systems. For a flame retardant to be of any use in this type of application it must have a high degree of chemical stability, in order to prevent reaction with the amine catalysts or hydrolysis on contact with water. The most suitable flame retardant to impart long term system stability in two component polyol preblends is AMGARD TMCP (Albright & Wilson), Tris(chloropropyl) phosphate.

5.1.5.2.3 Spray Foams

The main application of spray foams is for cavity wall insulation. Most spray foams are based on aromatic amine polyether polyols. These polyols are ideally suited to spray applications due to their extremely fast reactivity. The catalysts used for spray foam applications are usually metal salts, either dibutyl tin dilaurate or lead naphthenate in order to work in cold climates.

A major problem with spray foam systems, encountered in attempting to replace CFC blowing agents, is the increase in viscosity of the components. A lot of work has been done in developing lower viscosity polyols in response to the demand for partial or all water blown foams.

5.1.5.2.4 One Component Foams

One component foams are produced by manufacturing a prepolymer of MDI. The usual method involves reacting a polyether polyol with an excess of isocyanate dissolved in a low boiling point solvent. The catalysts used are often those used for flexible polyester foam formulations, N–ethylmorpholine and N–cetyldimethylamine. These catalysts are chosen to give one component foams long shelf lives. One component foams are typically dispersed from aerosol cans. The low boiling point solvent causes the contents to expand after which atmospheric moisture reacts with the excess isocyanate to give a fully cured foam. The addition of flame retardants to these systems serves as a plasticizer, to keep the finished foam slightly flexible.

5.2 Preliminary Flammability Testing Of 1–Methoxy–3–Methyl –2–Phospholene Oxide As A Flame Retardant In Polyurethane Foam Formulations

The first novel compound synthesised, 1–methoxy–3–methyl –2 phospholene oxide was initially tested as a flame retardant, in both rigid and flexible polyurethane foams. Each test being compared to a known leading flame retardant.

The flexible foam formulation used is listed below.

Component		Grammes
Con Polyol 48.0 OHV : Shell Caradol 48.2		1000
TDI 110 index : Toluene Diisocyanate		523
Water		41.5
Amine	1.2g Air Products DABCO 33LU	1.6
	0.4g Union Carbide NIAX AI	
Stannous Octoate		2.5
Silicone : Goldschmidt Tegostab BF 2370		13
Flame Retardant :		60, 80, 100 & 120

Amgard V6 (high molecular weight organophosphate)

or **1-methoxy-3-methyl-2-phospholene oxide (MMPO)**

For each formulation, the water, amine, silicone, polyol, and flame retardant were mixed together. As the unstable stannous octoate catalyst reacts with water it was added during stirring. Finally toluene diisocyanate (TDI) was added, the mixture stirred, poured into a 2' x 2' x 1' mould and then left overnight. The different loadings (levels of addition) of the flame retardant 1–methoxy–3–methyl–2–phospholene oxide (termed MMPO in the tests) were used to investigate whether the amount of flame

retardant affected the overall flammability performance of the foam. There are certain specific events that occur during the "foaming" reaction. The times at which these events occurred were recorded to assess the effect of the novel flame retardant on the foam formulation, when compared to that of the reference flame retardant on the foam formulation. These specific time events are explained below.

- The ***cream time*** is the time taken from the mixing of the components of the foam formulation to the time when they start to react together (associated with a reduction in the intensity of the colour of the reactants and the so called "creaming"). Normally the isocyanate (in this case either TDI or MDI) is added to the other ingredients and they are mixed thoroughly with an overhead stirrer and the reaction mixture is then poured quickly in to the mould.

- The ***gel time*** is the time taken for the developing foam to become "tacky".

- The ***rise time*** is the time taken for the developing foam to attain full development.

- The ***set time*** is the time taken for the fully developed foam to attain a "skin".

The times described above, for both the control flame retardant of Amgard V6 and the novel compound MMPO at various loadings are listed overleaf.

With the control of Amgard V6 (reference flame retardant) at 6 parts per hundred grammes of polyol (60 grammes) :

Cream time 18 seconds

Gel time 80 seconds

Rise time 99 seconds

Set time 101 seconds

With MMPO at 6 parts :

Cream time 21 seconds

Gel time 106 seconds

Rise time 145 seconds

But the foam collapsed internally, as if there was no cross linking of the polyol, when it was removed from the mould. Thus no set time was determined.

With MMPO at 8 parts :

Cream time 21 seconds

Gel time 110 seconds

Rise time 150 seconds

The same internal foam collapse occurred as before, when the foam was removed from the mould. Loadings of MMPO at 10 and 12 parts also had the same end result. It appeared that with the flame retardant MMPO, something was affecting the cell structure of the flexible polyurethane foam preventing the foam cells from binding together. The identical result happened with each of the "scorch" test blocks formulated, even though the amount of the flame retardant and consequentially any impurity or deleterious effect was small. A "scorch" block flexible foam formulation consists of 100g polyether, 54g TDI, 4g water, 1.12g amine, 1g surfactant, 0.25g tin catalyst and 21.1g flame retardant. "Scorch" blocks are a method

of assessing the scorching effect of the flame retardant and use a fraction of each foam component to produce miniature blocks of foam based on the same formulations used for the large scale foam blocks. Possible causes of the foam collapsing incident, however improbable, are listed below.

1: Acidity value of the flame retardant — normally effects the gel structure not cell structure.
2: Impurity in flame retardant — a 10% methylene chloride impurity would cause the foam to be overblown. Other impurities might have similar effects and they need not be present in any great quantities (in particular trace metal ions can have damaging catalytic effects). Teflon seals were used for all glassware joints in the preparation of the compounds, as minute quantities of silicone grease can have detrimental effects on foam formulations.
3: The flame retardant itself could be incompatible — this is unlikely, but not impossible, as there seems no valid reason why the structure of MMPO should have caused this to happen.

Both methylene chloride and methanol (two potential impurities from the synthesis of MMPO) are very volatile and were removed from the product. Any slight residue remaining would evaporate off in a short time and so cannot be present as deleterious impurities causing the foam to collapse since both methylene chloride and methanol would need to be present in large quantities to have the observed effect. However the sodium hydrogen carbonate solution used in the extraction phase resulted in a small amount of a crystalline impurity (sodium chloride), which was removed by filtration from MMPO and so it may be possible that a trace amount of a sodium salt was still present in the product. But ^{23}Na NMR

did not confirm this, although a trace quantity undetectable by ^{23}Na NMR might have caused the observed result.

Another reason for the flexible foam's collapse could have been that the compound MMPO acted as a solvent for flexible polyurethane foams. Therefore a flexible foam solubility test was performed by placing a small piece of flexible foam in the flame retardant MMPO and noting any deterioration in the foam's structure. After two weeks' immersion there was no significantly appreciable deterioration of the foam. Therefore MMPO was not a solvent for flexible polyurethane foams and so the observed effect with flexible foams is due to a different reason. A highly purified quantity (about 150 grammes) of 1–methoxy–3–methyl–2–phospholene oxide was prepared by distillation to ascertain if trace sodium metal ions (or indeed any trace impurity, e.g. from residues on glassware used) were responsible for the collapsing effect. When this highly purified form of 1–methoxy–3–methyl–2–phospholene oxide was used in a similar flexible foam formulation, the same collapsing result was still observed, with the foam being poisoned after the normal set time; cream times and gel times were as before.

Since the flexible foam formulation met with disaster, a rigid foam formulation was tried. Rigid foams tend to be a lot less sensitive to incompatibility problems than flexible foams and consequently are a lot more "forgiving" to impurities, acidity values and slight incompatibilities.

The rigid foam formulation used is detailed below.

Component	Grammes
Polyol : ARCO ARCOL 3758	500
MDI Lupranate M20S : Methyl Diisocyanate	912.3
Water	2.5
DMCHA : Dimethyl Cyclohexylamine	7.5
Surfactant : Air Products DABCO DC193	5
Arcton 11 : Trichlorofluoromethane	175
Flame Retardant : DMMP or MMPO	60

With control of DMMP (a low molecular weight alkyl phosphonate) at 12 parts per hundred grammes of polyol (60 grammes) :

Cream time 23 seconds

Gel time 46 seconds

Rise time 57 seconds

Set time 60 seconds

With MMPO at 12 parts :

Cream time 23 seconds

Gel time 48 seconds

Rise time 58 seconds

Set time 77 seconds

This time the foam retained its structure upon removal from the mould and so flammability tests could be performed.

5.3 Preliminary Flammability Testing Of 1–Methoxy–3–Methyl–2–Phospholene Oxide Loaded Rigid Polyurethane Foam

Density of rigid foam containing DMMP : 28.2 kg m^{-3}

Density of rigid foam containing MMPO : 24.4 kg m^{-3}

This significant reduction in density suggests that a slight overblowing effect had occurred and scorching was also observed. The scorching is caused by dehydrogenation, attributable to an acidic species. The initial flammability test performed was the standard DIN 4102 test, 5 edge tests and 5 surface exposure tests, the flame being applied for 15 seconds, as shown in Figure 49.

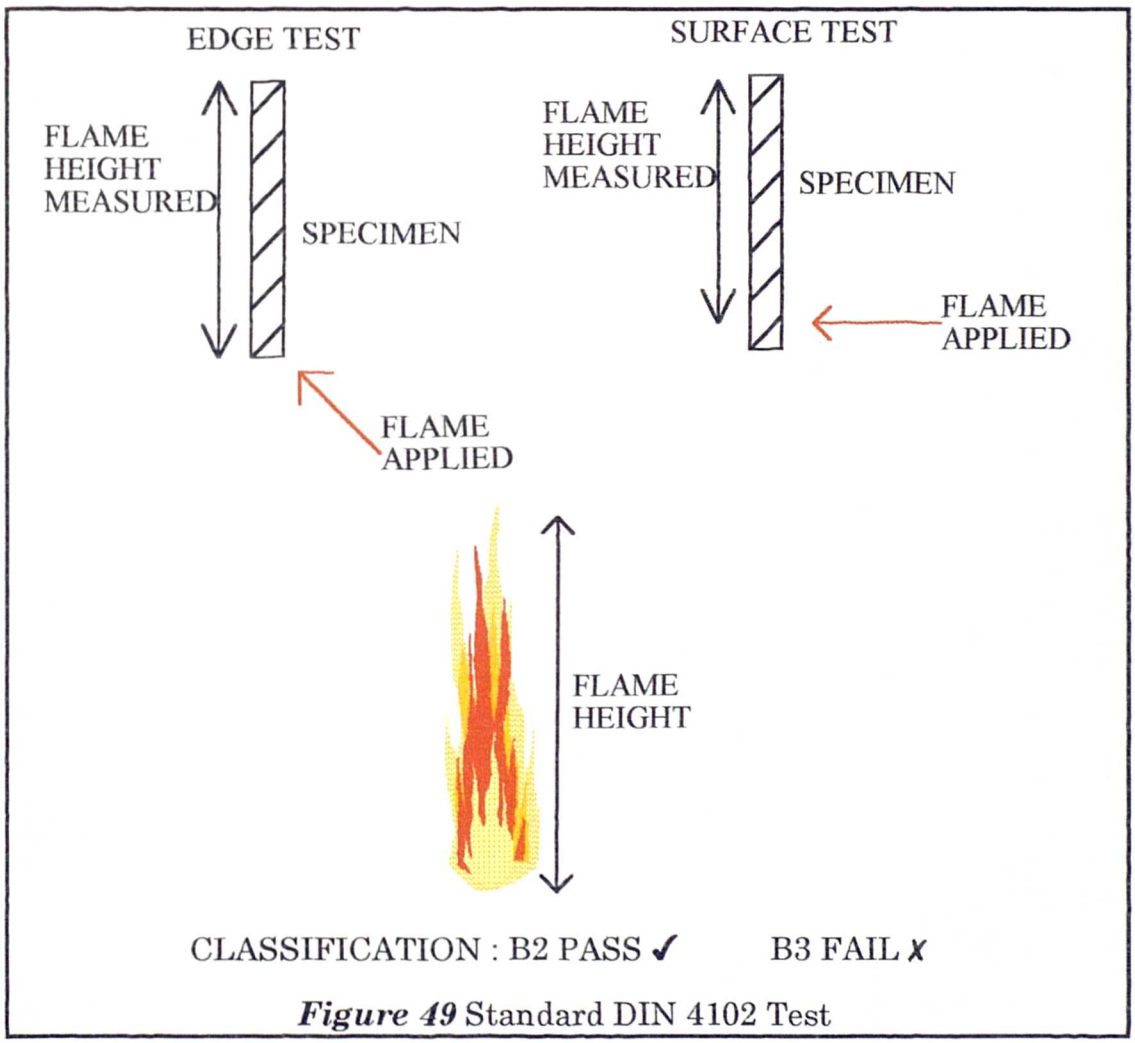


Figure 49 Standard DIN 4102 Test

The specimen foam was cut up into test pieces measuring 230 mm x 90 mm x 25 mm. To pass the test a flame height of less than 150 mm must be observed.

DMMP (market leader in rigid foam flame retardants) at 12 parts

Edge tests

130 mm	120 mm	120 mm	120 mm	120 mm

Average : **122 mm** PASS ✓

Surface tests

110 mm	120 mm	120 mm	100 mm	110 mm

Average : **112 mm** PASS ✓

MMPO at 12 parts

Edge tests

130 mm	140 mm	130 mm	130 mm	140 mm

Average : **134 mm** PASS ✓

Surface tests

120 mm	120 mm	120 mm	120 mm	130 mm

Average : **122 mm** PASS ✓

When compared to the average flame height for the control flame retardant DMMP, the test flame retardant MMPO performed adequately, the recorded flame heights being well below 150 mm.

These results demonstrated that there was good potential in phospholene oxide esters as acceptable flame retardants for polyurethane foams, performing almost as well as the market leader DMMP, a low molecular weight alkyl phosphonate. Full scale testing of the four phospholene oxide esters synthesised as flame retardants in polyurethane foams was then performed.

5.4 Full Scale Flammability Testing Of Four Phospholene Oxide Esters Synthesised

All of the phospholene oxide esters synthesised, 1–Methoxy–3–Methyl 2–Phospholene Oxide (MMPO : 21.2% Phosphorus), 1–Ethoxy–3 Methyl 2 Phospholene Oxide (EMPO : 19.4% Phosphorus), 1–Isopropoxy 3 Methyl 2–Phospholene Oxide (IMPO : 17.8% Phosphorus) and 1–Tertbutoxy–3 Methyl–2–Phospholene Oxide (TBMPO : 16.4% Phosphorus) were initially incorporated into a flexible foam formulation, but the flexible foam's internal cell structure collapsed as before. An interesting fact observed was that the flexible foam's cell structure was retained to a greater degree as the phospholene oxide molecular weight increased from MMPO to TBMPO, although the foams loaded with TBMPO still collapsed. That the flexible foam loaded with TBMPO almost "held" together, suggested that it was the thermal stability of the phospholene oxides and their consequent partial decomposition products that were affecting the foam structure and causing the foam's cell structure to collapse. The core temperatures generated within flexible foams as they form can exceed 180°C. It would appear most likely that the foam collapse problem was caused by decomposition of the phospholene oxide itself rather than any trace impurities.

The four flame retardants were successfully incorporated into rigid foam formulations at 14 parts, 16 parts and 18 parts. These levels of loadings were chosen because the loading used for commercial flame retardants is 15 parts. It was observed that there was a reaction occurring between the amine catalyst dimethyl cyclohexylamine and two of the flame retardants IMPO and TBMPO. This did not however appear to affect the formation or stability of the foam. The formulation used for the rigid foam is shown overleaf.

Component	Grammes
Polyol : ARCO ARCOL 3758	500
MDI Lupranate M20S : Methyl Diisocyanate	912.3
Secondary blowing agent : Water	2.5
Amine Catalyst : DMCHA : Dimethyl Cyclohexylamine	7.5
Surfactant : Air Products DABCO DC193	5
Blowing Agent : Arcton 11 : Trichlorofluoromethane	175
Flame Retardant :	70 – 90 (14 – 18 parts)

Upon cutting the foams, a pungent aroma was detected and scorching seen, scorching is caused by dehydrogenation, attributable to the presence of an acidic species. However both the aromas and scorching reduced with each successive foam formulation. With TBMPO no scorching and no aroma were detected. It would therefore seem likely that this scorching and pungent aroma was associated with the boiling point and or thermal stability of the phospholene oxides; TBMPO has the highest boiling point (135°C) and MMPO the lowest boiling point (70°C).

The core temperature of rigid foams during manufacture exceeds 160°C, this may therefore result in a partial decomposition of the phospholene oxides with lower boiling points and possibly lower thermal stability. Thus an acidic species is generated giving rise to the scorching seen in three of the foam batches. The pungent aroma would thus appear to be the result of the partial decomposition forming an acidic species, obviously some form of phosphorus oxide (PO_x), see Figure 50.

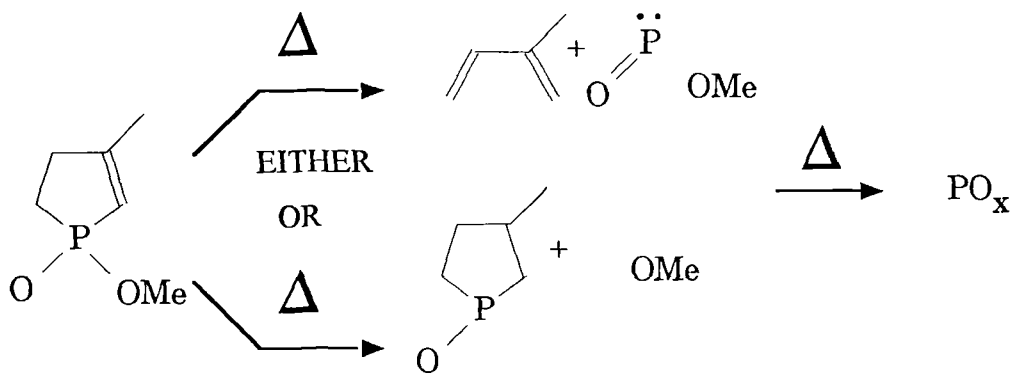


Figure 50 Possible Decomposition Products Of MMPO

The pungent aroma accompanying the scorching seen, arises because of the excellent gas impermeable properties of rigid polyurethane foams trapping this aroma within its closed cell structure and releasing it when cut.

The rigid foams' cell structures are obviously less susceptible than the flexible foam structure to the "poisoning" effect of these acidic decomposition products and so do not collapse. However the presence of these acidic decomposition products is indicated by the scorching seen and the pungent aroma detected upon cutting the foam. Differential scanning calorimetry was later used to establish the thermal stability of the novel phospholene oxide compounds.

Table 5.5 lists the formulation times for each of the rigid foams synthesised at the various loadings of each flame retardant.

Table 5.5 Formulation Times for Rigid Foams Synthesised

Parts Of Flame Retardant	Cream Time (secs)	Gel Time (secs)	Rise Time (secs)	Set Time (secs)
14 DMMP	22	45	58	64
14 MMPO	17	41	59	60
16 MMPO	17	42	58	59
18 MMPO	16	35	55	56
14 EMPO	19	40	57	58
16 EMPO	17	39	57	58
18 EMPO	18	37	52	53
14 IMPO	22	49	72	73
16 IMPO	21	49	72	73
18 IMPO	20	49	67	68
14 TBMPO	18	49	69	70
16 TBMPO	22	49	65	66
18 TBMPO	20	48	65	66

The density for each of the foams produced are given below.

Density of rigid foam containing DMMP at 14 parts :	28.8 kg m^{-3}
Density of rigid foam containing MMPO at 14 parts :	24.1 kg m^{-3}
Density of rigid foam containing MMPO at 16 parts :	24.5 kg m^{-3}
Density of rigid foam containing MMPO at 18 parts :	24.9 kg m^{-3}
Density of rigid foam containing EMPO at 14 parts :	26.3 kg m^{-3}
Density of rigid foam containing EMPO at 16 parts :	27.1 kg m^{-3}
Density of rigid foam containing EMPO at 18 parts :	27.2 kg m^{-3}
Density of rigid foam containing IMPO at 14 parts :	26.2 kg m^{-3}
Density of rigid foam containing IMPO at 16 parts :	25.6 kg m^{-3}
Density of rigid foam containing IMPO at 18 parts :	25.4 kg m^{-3}
Density of rigid foam containing TBMPO at 14 parts :	22.4 kg m^{-3}
Density of rigid foam containing TBMPO at 16 parts :	21.6 kg m^{-3}
Density of rigid foam containing TBMPO at 18 parts :	20.5 kg m^{-3}

All the foams have a lower density than the DMMP loaded foam, with the TBMPO loaded foam having the lowest density of all. There is no significant reduction in density for either EMPO or IMPO indicating that there is no significant overblowing. However with MMPO there is an overblowing effect occurring, even more so with TBMPO. This is strange as TBMPO has the highest boiling point of the four phospholene oxides and it was expected that the MMPO loaded foam would have the lowest density as MMPO has the lowest boiling point.

5.5 Full Scale Flammability Testing

The first flammability test to be performed was the DIN 4102 surface and edge flammability test.

5.5.1 DIN 4102 Surface And Edge Flammability Test

The first flammability test performed was the standard DIN 4102 B2/B3 test as before.

DMMP at 14 parts

Edge test

130 mm 135 mm 130 mm 120 mm 125 mm

Average : **128 mm** PASS ✓

Surface test

115 mm 120 mm 125 mm 110 mm 120 mm

Average : **118 mm** PASS ✓

MMPO at 14 parts

Edge test

130 mm 130 mm 130 mm 140 mm 140 mm

Average : **134 mm** PASS ✓

Surface test

110 mm 110 mm 120 mm 110 mm 120 mm

Average : **114 mm** PASS ✓

MMPO at 16 parts

Edge test

125 mm	130 mm	120 mm	135 mm	130 mm

Average : **128 mm** PASS ✓

Surface test

110 mm	110 mm	110 mm	110 mm	110 mm

Average : **110 mm** PASS ✓

MMPO at 18 parts

Edge test

120 mm	120 mm	110 mm	120 mm	130 mm

Average : **120 mm** PASS ✓

Surface test

110 mm	100 mm	110 mm	110 mm	120 mm

Average : **110 mm** PASS ✓

EMPO at 14 parts

Edge test

140 mm	140 mm	120 mm	120 mm	120 mm

Average : **128 mm** PASS ✓

Surface test

110 mm	120 mm	130 mm	120 mm	110 mm

Average : **118 mm** PASS ✓

EMPO at 16 parts

Edge tests

110 mm	120 mm	110 mm	115 mm	110 mm

Average : **113 mm** PASS ✓

Surface tests

110 mm	110 mm	120 mm	120 mm	110 mm

Average : **114 mm** PASS ✓

EMPO at 18 parts

Edge tests

120 mm	140 mm	130 mm	140 mm	130 mm

Average : **132 mm** PASS ✓

Surface tests

110 mm	120 mm	110 mm	110 mm	110 mm

Average : **112 mm** PASS ✓

IMPO at 14 parts

Edge tests

90 mm	110 mm	100 mm	120 mm	110 mm

Average : **106 mm** PASS ✓

Surface tests

120 mm	120 mm	120 mm	120 mm	120 mm

Average : **120 mm** PASS ✓

IMPO at 16 parts

Edge tests

120 mm	110 mm	110 mm	100 mm	100 mm

Average : **108 mm** PASS ✓

Surface tests

120 mm	120 mm	120 mm	120 mm	110 mm

Average : **118 mm** PASS ✓

IMPO at 18 parts

Edge tests

110 mm	110 mm	110 mm	100 mm	100 mm

Average : **106 mm** PASS ✓

Surface tests

110 mm	110 mm	120 mm	120 mm	110 mm

Average : **114 mm** PASS ✓

TBMPO at 14 parts

Edge tests

>150 mm	>150 mm	>150 mm	>150 mm	>150 mm

Average : **>150 mm** FAIL ✗

Surface tests

>150 mm	>150 mm	>150 mm	>150 mm	>150 mm

Average : **>150 mm** FAIL ✗

TBMPO at 16 parts

Edge tests

>150 mm >150 mm >150 mm >150 mm >150 mm

Average : **>150 mm** FAIL ✗

Surface tests

>150 mm >150 mm >150 mm >150 mm >150 mm

Average : **>150 mm** FAIL ✗

TBMPO at 18 parts

Edge tests

>150 mm >150 mm >150 mm >150 mm >150 mm

Average : **>150 mm** FAIL ✗

Surface tests

>150 mm >150 mm >150 mm >150 mm >150 mm

Average : **>150 mm** FAIL ✗

5.5.2 Epiradeateur Flammability Test

The subsequent test performed was the Epiradeateur test NF P 92–501 shown in Figure 51. This is the basic method of classifying the fire performance of rigid materials of any thickness in France. The test may also be used on flexible materials more than 5 mm thick. This test requires a minimum of four specimens of 300 mm x 400 mm x 50 mm. Each sample is mounted in turn at 45° angle over and parallel to a 500 W electric radiator. The specimen is 30 mm distant from the radiator and receives 3 W cm^{-2} of radiant energy over its lower part. Two butane gas ignition sources are applied, one to the lower and one to the upper surface of the specimen. The lower ignition source is a burner in the shape of an

arc of a circle; the upper ignition source is a rectangular burner 60 mm long.

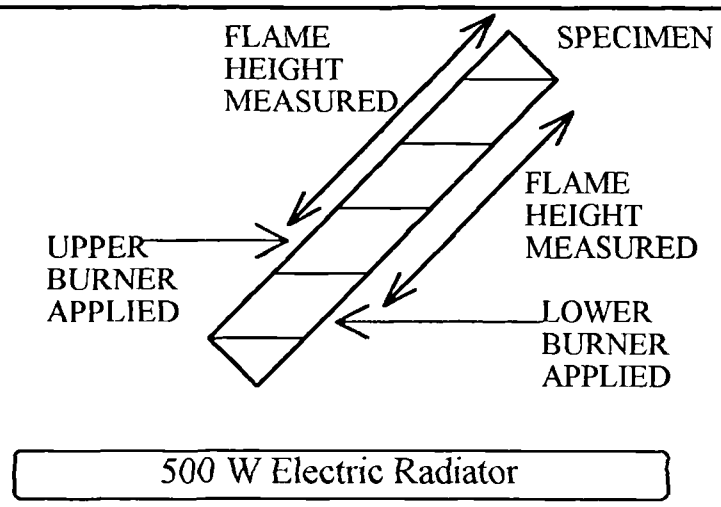


Figure 51 The Epiradeateur Test

Depending on the onset, height and duration of flaming combustion, the rise in temperature above the specimen, and on secondary effects such as the level of smoke generation and the presence of burning droplets, after glowing and after flaming, the material is classified in five classes of increasing combustibility from M1 to M5. Materials that fail to reach classes M1, M2 or M3 are subjected to a laboratory scale spread of flame test, NF P 92 504. This is a simple horizontal burning test in which a Bunsen flame is applied to the free end of a 300mm x 400mm x 50mm specimen for 30 seconds and the rate of burning determined.

The material is classified M4 if it passes this test and M5 if it fails this test.

During the test the following are noted :

1) The ignition time (time elapsed between the beginning of the test and ignition), t_1 and t_2 for the lower and upper faces of the specimen. The

ignition of the gas released by the specimen is only considered as effected if it is maintained for at least 5 seconds.

2) When ignition of the specimen has occurred the burning device should be removed from the appropriate face, the ignition times t_1 and t_2 are measured one second after ignition. The burning device is only replaced when the gas flame has extinguished. If the sample ignites several times during the course of the test, the burning device should be removed each time and replaced after each extinction.

3) After each 30 second interval the flame height attained is noted. Measurement of the flame height is facilitated by marked intervals of 30mm made on the support frame.

The following additional observations are also noted :

- any superficial changes on either side of the specimen, deformation of the specimen.
- any smoke evolution.
- drops of material on the radiator and their ignition.
- continuation of combustion with or without flaming after the end of the test.
- any dangerous property displayed by the material, i.e. loss of weight after cooling, and the dimensions of the charred area on each face of the specimen.

Specimen test sheets are shown in Tables 5.6 and 5.7, with the results for all the specimens shown in Table 5.9.

Table 5.6 Epiradeateur Test Results For MMPO At 14 Parts

	Length of flames in centimetres	
Time in seconds	Upper Surface	Lower Surface
0	0	0
30	0	21
60	0	18
90	0	18
120	0	18
150	21	0
180	6	0
210	3	0
240	0	0
270	0	0
300	0	0
330	0	0
360	0	0
390	0	0
420	0	0
450	0	0
480	0	0
510	0	0
540	0	0
570	0	0
600	0	0
630	0	0
660	0	0
690	0	0
720	0	0
750	0	0
780	0	0
810	0	0
840	0	0
870	0	0
900	0	0
930	0	0
960	0	0
990	0	0
1020	0	0
1050	0	0
1080	0	0
1110	0	0
1140	0	0
1170	0	0

Sum of flame lengths : 30 + 75 =105

Table 5.6 Continued

Duration of non–flaming of lower face (ignition time) t_1 : **25** seconds

Duration of non–flaming of upper face (ignition time) t_2 : **132** seconds

Ignition Index i : **3.17**

Development Index s : **0.75**

Maximum Flame Length Index h : **1.05**

Reaction to Fire of Specimen : The material burned readily for a short time (< 10 seconds) and then the flame diminished and finally extinguished after 3 minutes, leaving a significant amount of charring evident on both surfaces.

Observations : Black smoke evolved from specimen accompanied by some fine particulates in the smoke. Large amount of charring was evident on each surface, no deformation of the specimen.

CLASSIFICATION : M3

Table 5.7 Epiradeateur Test results For TBMPO At 18 Parts

	Length of flames in centimetres	
Time in seconds	Upper Surface	Lower Surface
0	0	0
30	0	>21
60	0	21
90	0	18
120	>21	0
150	21	0
180	9	0
210	0	0
240	0	0
270	0	0
300	0	0
330	0	0
360	0	0
390	0	0
420	0	0
450	0	0
480	0	0
510	0	0
540	0	0
570	0	0
600	0	0
630	0	0
660	0	0
690	0	0
720	0	0
750	0	0
780	0	0
810	0	0
840	0	0
870	0	0
900	0	0
930	0	0
960	0	0
990	0	0
1020	0	0
1050	0	0
1080	0	0
1110	0	0
1140	0	0
1170	0	0
Sum of flame lengths	> 51	> 60 ≥ 111

Table 5.7 Continued

Duration of non–flaming of lower face t_1 : **15** seconds

Duration of non–flaming of upper face t_2 : **105** seconds

Ignition Index i : **5.08**

Development Index s : **> 0.8**

Maximum Flame Length Index h : **> 1.05**

Reaction to Fire of Specimen : The material burned readily for a short time (< 30 seconds) and then the flame diminished and finally extinguished after 3 minutes, leaving a significant amount of charring evident on both surfaces. For a brief time the flame height exceeded 21cm and therefore could not be measured on the test rig, since the flames went past the marked intervals on the support frame. Even if all other parameters could be recorded and the specimen appeared to comply with an M3 specification it is unwise and wrong to classify the specimen as M3. In such cases the NF P 92–504 test, a simple flame spread test, is then performed to classify the specimen as M4 or M5.

Observations : Flames from specimen extended beyond the support frame for a brief time (< 15 seconds) on both lower and upper surfaces. Black smoke evolved from specimen accompanied by some fine particulates in the smoke. Large amount of charring evident on each surface, no deformation of the specimen.

CLASSIFICATION : M4

The results shown in those two tables are calculated as shown below, with the specifications illustrated in Table 5.8.

Calculation of indices : Indices are calculated from the results recorded on the test sheet for each specimen as follows :

IGNITION INDEX : i

$$i = \frac{1000}{15t_1} + \frac{1000}{15t_2}$$

where t_1 and t_2 are the ignition times for the lower and upper faces in seconds.

DEVELOPMENT INDEX : s

This is the sum of the maximum flame lengths in centimetres measured at 30 second intervals all divided by 140.

MAXIMUM FLAME LENGTH INDEX : h

This is the maximum flame length in centimetres divided by 20.

Table 5.8 Specifications For The Epiradeateur Test

Classification	i	s	h
M1	0	0	0
M2	(i) anything	<0.2	<1
	(ii) <1	0.2–1.0	<1
M3	(i) anything	0.2–1.0	<1
	(ii) <2	1–5	<2.5

M4 None of the above and a rate of flame propagation <2mm/sec

M5 None of the above and a rate of flame propagation >2mm/sec

Table 5.9 Epiradeateur Test Results For All Specimens

Average of four 20 minute tests for each sample :

Parts	Ignition Index i	Development Index s	Maximum Flame Length Index h	Classification
14 MMPO	3.17	0.75	1.05	**M3**
16 MMPO	2.85	0.58	1.05	**M3**
18 MMPO	2.38	0.41	1.05	**M3**
14 EMPO	3.6	0.80	>1.05	M4
16 EMPO	3.3	0.78	1.05	**M3**
18 EMPO	2.93	0.74	1.05	**M3**
14 IMPO	3.8	0.80	>1.05	M4
16 IMPO	3.7	0.79	>1.05	M4
18 IMPO	3.5	0.76	>1.05	M4
14 TBMPO	4.1	0.79	>1.05	M4
16 TBMPO	3.8	0.75	>1.05	M4
18 TBMPO	3.6	0.73	>1.05	*M4*

At conventional loadings, DMMP (reference flame retardant) treated rigid foams receive an M4 classification.

It must be remembered that these phospholene oxide flame retardants are entirely phosphorus based and will therefore function only in the condensed phase (see sections 1.4 & 1.7.1). Their method of flame retardant action will rely solely on the formation of char as a barrier to further combustion. They will not function in the vapour phase, inhibiting the flame chemistry as halogenated flame retardants would. Thus one would expect to see an initial period during which the material burns readily and then as char formation increases the flames will extinguish

and then no further combustion will occur. This was indeed exactly what was seen. With the higher phosphorus containing phospholene oxides the char formation was very significant and effective in retarding the flame spread. It was this initial flame spread that was markedly controlled by the particular phospholene oxide present. All the phospholene oxides at all loadings effectively extinguished the flames through char formation after 3 minutes. At the lowest loadings of TBMPO (i.e. lowest possible phosphorus content) the initial flame spread was quite dramatic and uncontrollable, with both surfaces rapidly engulfed in flames, but still extinguishing after 3 minutes. At the highest loadings of MMPO (i.e. highest possible phosphorus content) the initial flame spread is small and contained, with only the lower surface burning and again extinguishing after 3 minutes. There was a gradual increase in the flame spread going from high loadings to lower loadings of the phospholene oxides and going from MMPO to TBMPO. The boiling points of the phospholene oxides do not seem to affect their performance as flame retardants, only their compatibility with the foams.

5.5.3 Limiting Oxygen Index Test

The last flammability tests performed were limiting oxygen index studies. Limiting oxygen [Fenimore, C.P. 1966] index consists of ascertaining the minimum percentage of oxygen required to support sustained combustion. The test specimen is placed inside a glass chimney through which a controlled atmosphere, containing an adjustable amount of oxygen, ascends as shown in Figure 52. A source of ignition (gas burner flame) is applied to the specimen for ten seconds and the burning behaviour of the specimen observed. Adjustments in oxygen concentration are then performed and the test is repeated until the specimen 'just'

burns. When this circumstance is attained the percentage of oxygen needed is termed the limiting oxygen index value for the test specimen. The test is repeated at the limiting oxygen index value a minimum of five times to validate the result. For polyurethane foams, the terminology 'just' burns is described as that level of oxygen which sustains combustion that does not consume more than 50 mm of the test specimen.

The test, referred to as the ASTM D–2863 test, specimen type C 12.5 mm x 12.5 mm x 125 mm, was performed on a Stanton Redcroft FTA Flammability Unit.

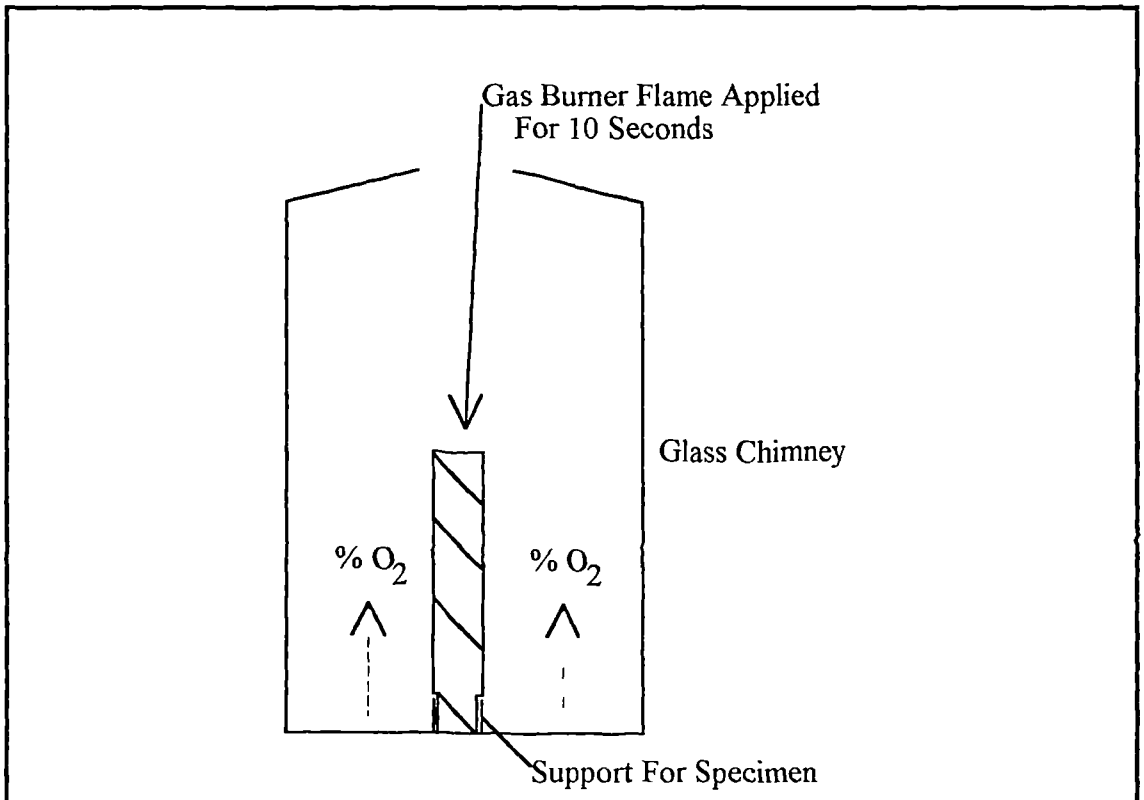


Figure 52 LOI Test Apparatus

The LOI'S of the four phospholene oxide esters, at each of the three loadings are recorded in Table 5.10. As expected the LOI value increases as the number of parts of flame retardant is increased. However, there is no apparent order on going from MMPO to TBMPO. Although the

percentage content of phosphorus decreases from MMPO to TBMPO, the absolute amount of phosphorus is dictated by the density of the particular foam. A more meaningful manner in which to ascertain the level of phosphorus for a particular foam is to calculate the comparative addition level of phosphorus, as shown in Table 5.11. The comparative phosphorus addition level is calculated by taking the percentage of phosphorus in a foam loaded at 14 parts MMPO as a standard (i.e. a value of 1.0). The percentage of phosphorus in all the other foams is then calculated with reference to this standard, by using the respective relative atomic and relative molecular weights.

Table 5.10 LOI'S (% oxygen) For Each Novel Flame Retarded Foam

	Parts		
FR Foam	14	16	18
MMPO	23.0	23.9	24.8
EMPO	23.1	24.2	24.5
IMPO	22.8	23.3	23.8
TBMPO	<20.9	21.8	21.9

Table 5.11 Comparative Phosphorus Addition Level (Percentage Phosphorus) For Each Novel Flame Retarded Foam

Foam containing MMPO at 14 parts taken as standard.

	Parts		
FR Foam	14	16	18
MMPO	1.00	1.14	1.29
EMPO	0.92	1.04	1.13
IMPO	0.84	0.95	1.07
TBMPO	0.78	0.89	1.00

If these values in Table 5.11 are then multiplied by the particular densities for each foam, shown in Table 5.12, then a measure of the relative phosphorus content in each foam is obtained. This relative phosphorus content is shown in Table 5.13.

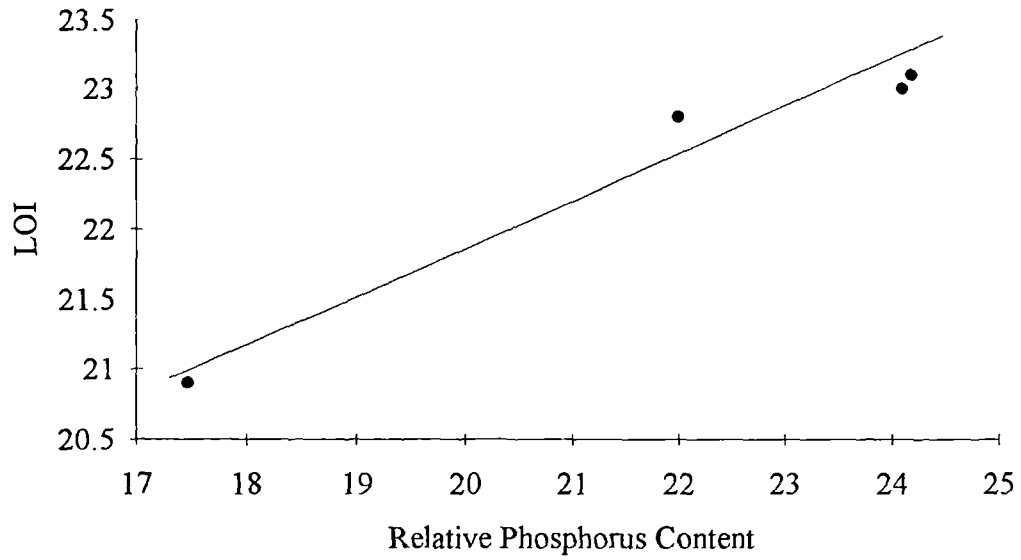
Table 5.12 Densities (kg m^{-3}) For Each Novel Flame Retarded Foam

	Parts		
FR Foam	**14**	**16**	**18**
MMPO	24.1	24.5	24.9
EMPO	26.3	27.1	27.2
IMPO	26.2	25.6	25.4
TBMPO	22.4	21.6	20.5

Table 5 13 Relative Phosphorus Content For Each Novel Flame Retarded Foam

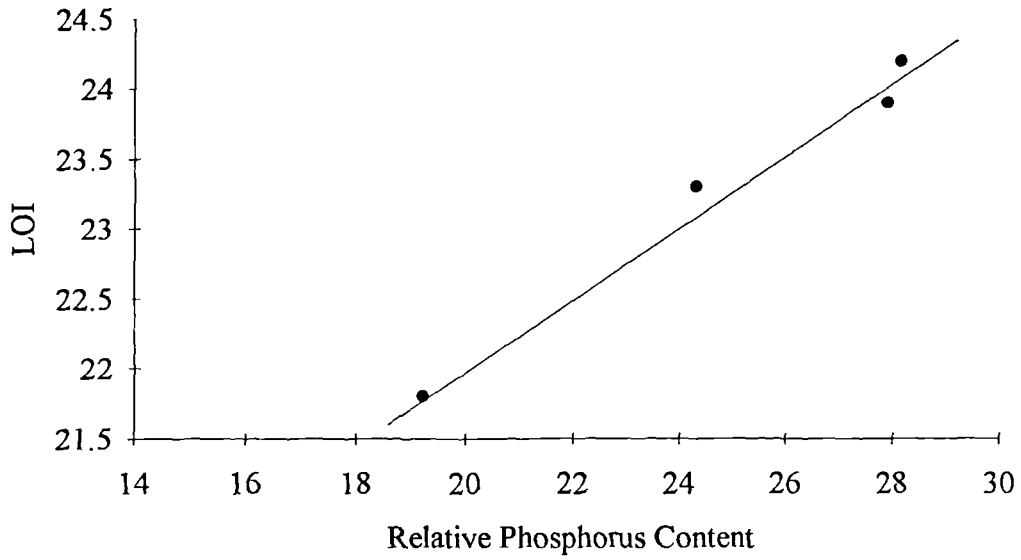
	Parts		
FR Foam	**14**	**16**	**18**
MMPO	24.1	27.93	32.12
EMPO	24.19	28.18	30.74
IMPO	22.0	24.32	27.18
TBMPO	17.47	19.22	20.5

The anomalies in the LOI values on going from MMPO to TBMPO are fully explained by these qualitative amounts. Statistical correlation exercises between the LOI values and the qualitative phosphorus contents, for the four flame retarded foams at each of the three loadings are shown in Figures 53 — 55. The correlation coefficients are all greater



Correlation coefficient R = 0.977

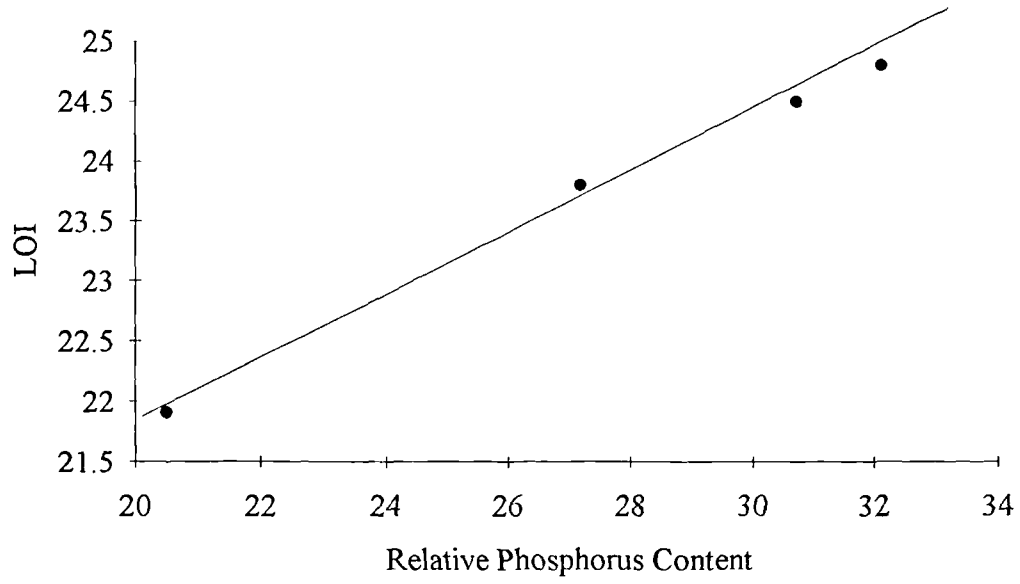
Figure 53 Correlation Of LOI'S With Relative Phosphorus Content For Foams Loaded At 14 Parts Of Novel Flame Retardant



Correlation Coefficient R = 0.991

Figure 54 Correlation Of LOI'S With Relative Phosphorus Content For Foams Loaded At 16 Parts Of Novel Flame Retardant

than 0.97, indicating an accurate correlation between the LOI results and the phosphorus content in the phospholene oxide ester flame retardants.



Correlation Coefficient R = 0.996

Figure 55 Correlation Of LOI'S With Relative Phosphorus Content For Foams Loaded At 18 Parts Of Novel Flame Retardant

It is only really valid to correlate values obtained for similar types of flame retardants, i.e. the phospholene oxide esters, and not other flame retardants as well. For instance the comparative phosphorus content for a foam loaded at 14 parts of the reference flame retardant DMMP is 1.18, its density is 28.8 kg m-3 and hence its relative phosphorus content is 34. Although its LOI value is 24.9 this would correlate badly with the other values. It also received an M4 classification in the Epiradeateur test.

Using this relative phosphorus content level as a guide the Epiradeateur test results in Table 5.9 can be explained. As shown in Table 5.14, excepting MMPO at 14 parts it would seem that a qualitative phosphorus content level of at least 28 is required to achieve an M3

classification. MMPO at 14 parts received an M3 classification yet EMPO at 14 parts and IMPO at 16 parts and 18 parts received an M4 classification even thought the latter three have a higher qualitative phosphorus content. This indicates that the alkyl ester group also plays an important part in the flame retardant behaviour of the novel compounds and not just the phosphorus content.

Table 5.14 Epiradeateur Test Results For All Specimens And Relative Phosphorus Contents

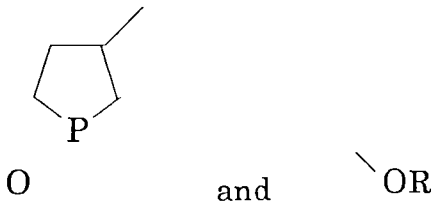
Parts	Classification	Relative Phosphorus Content
14 MMPO	**M3**	*24.1*
16 MMPO	**M3**	**27.93**
18 MMPO	**M3**	32.12
14 EMPO	M4	24.19
16 EMPO	**M3**	**28.18**
18 EMPO	**M3**	**30.74**
14 IMPO	M4	22
16 IMPO	M4	24.32
18 IMPO	M4	27.18
14 TBMPO	M4	17.47
16 TBMPO	M4	19.22
18 TBMPO	M4	20.5

6.0 Thermal Stability Of Phospholene Oxide Esters

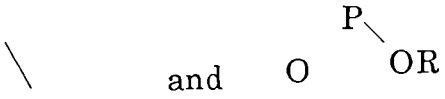
Differential Scanning Calorimetry (DSC) [Dodd, J.W. 1987] was used to investigate the thermal behaviour of the four phospholene oxide esters. The DSC traces obtained are shown in Figures 57 — 62. Differential Scanning Calorimetry was performed on a Mettler instrument with a TC10A processor. The weighed sample is sealed in a small aluminium pan (the sample pan lid is usually pierced to allow any gases evolved to escape) and placed in the DSC cell on a thermocouple, alongside a reference pan, the cell is then exposed to a controlled atmosphere whilst the analysis is performed. The instrument measures the enthalpy change (ΔH) undergone by the sample under investigation over the programmed temperature range. A DSC instrument measures the power difference required to maintain a reference specimen (usually either empty or dead burnt alumina) and the sample, at the same temperature whilst they are both heated at identical rates under the same conditions. Therefore the problem of heat loss from either the sample or the reference is negated because both the sample and reference are at the same temperature. DSC is a more sensitive technique than Differential Thermal Analysis (DTA) as the latter technique relies on a temperature difference between reference and sample to produce an output. With DTA heat losses are not accounted for since the sample and reference are at different temperatures. However with a power compensator DSC, any volatiles escaping can condense on the cell walls of the DSC as they are cooler than the sample pans. These condensing volatiles will cause the output signal to be subjected to a baseline shift, usually an endothermic shift. Thus if the sample pan is perforated with a single hole then any gaseous products can evaporate (endothermic process), escape and condense on the cooler cell walls of the DSC cell. This will result in an overall endothermic shift of the baseline

of the output trace. When the sample pan is sealed then no volatiles can escape and so the endothermic baseline shift does not occur and the evaporation and condensation within the sealed pan compensate each other [Dodd, J.W. 1987].

The DSC analysis was carried out under static air, to best mimic the conditions found in the making of the foam. The programmed temperature range was 25°C — 240°C, analogous to the temperatures found within the foaming mixture when making foams. Two types of sample pan configuration were used i.e. sealed and the lid perforated with a single hole. The two sample pan configurations gave two different DSC traces for each of the phospholene oxide esters examined, as presented in Figures 57 – 62. The traces from the sealed pans showed large endotherms, after 200°C, which were absent on the traces for the perforated pans. However, as shown in Figures 57 — 62, there are large exotherms in the region 100°C — 200°C for all the phospholene oxide esters and for both types of pan configuration. These are attributed to the phospholene oxide esters decomposing, by one or both of two possible mechanisms. The first, Mechanism I generates the two products



which decompose further into phosphorus oxides (PO_x). The alternative, Mechanism II generates the two products

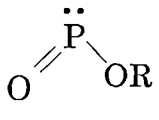
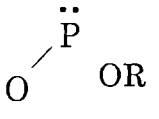


which decompose further into phosphorus oxides (PO_x) as was also the case for Mechanism I. Either of these two suggested mechanisms are

possible. Due to the inherent ring strain in phospholene oxides, it is more likely however that the ring structure would break apart (Mechanism II) and thus give the phosphorus oxide ester as opposed to remaining intact as a phospholene oxide (Mechanism I). Further evidence for Mechanism II is also provided from the conclusions drawn in the flammability test results reported in section 5.5, wherein it was shown that the alkyl ester group plays an important part in the flame retardant performance of each phospholene oxide ester. This would not be the case if Mechanism I was predominant, because this would result in an identical phosphorus fragment regardless of the particular phospholene oxide ester.

For the sample pans perforated with a single hole, there appeared to be an initial exotherm peaking at around 150°C for each phospholene oxide ester followed by a second exotherm. The latter exotherm is readily seen with MMPO around 200°C (Figure 57) but only the beginning is visible for EMPO around 230°C (Figure 58). The onset of this second exotherm is present for IMPO and TBMPO, with the peak temperature occurring above 240°C, the highest temperature investigated.

- The boiling points of each the four phospholene oxide esters (all lower than 150°C) did not seem to effect the position of the first exotherm, it remained constant at around 150°C for each of the phospholene oxide esters.
- However the position of the second exotherm was shown to be dependent on the particular phospholene oxide ester. This indicated that this exotherm was attributable to a process that was specific to each phospholene oxide ester.

These two inferences suggest that decomposition to the intermediate product  is attributable to the first exotherm. Since this phosphorus oxide ester will be more stable the larger the size of the alkyl group R, then the second exotherm should appear at a consistently higher temperature as R increases in size. The second exotherm would then be attributable to decomposition of  to yield the final product PO_x.

Mechanism I has the same intermediate phosphorus decomposition product irrespective of the initial phospholene oxide ester, as the ring structure does not break apart. Therefore one would expect the position of the second exotherm to also remain constant, corresponding to the decomposition of this same fragment. The evidence from the DSC traces does not agree with this decomposition route, since the second exotherm appears at a consistently higher temperature for each successive phospholene oxide ester. The fact that this second exotherm appears at a consistently higher temperature as the alkyl ester group increases in size is in agreement with Mechanism II. Thus all the available evidence is consistent with the ring structure breaking apart, that is Mechanism II, which is given in Figure 56.

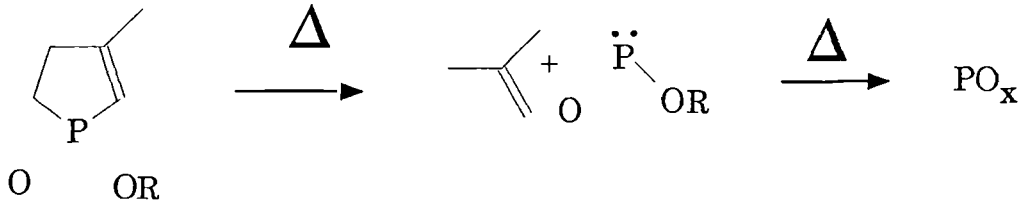


Figure 56 Mechanism Proposed For Decomposition Of Phospholene Oxide Ester

The extent of each exotherm was dependent on the particular phospholene oxide ester and the quantity present. The greatest exotherm being for MMPO, whereas a one third greater quantity of TBMPO produced a much smaller exotherm. For the samples in sealed pans, similar traces were seen with very large exotherms appearing in the region 100°C — 200°C. Each trace also showed a large endotherm occurring between 50° and 100°C and after 200°C. The exotherm occurs at successively higher temperatures with each phospholene oxide; TBMPO is the only exception with a large endotherm at < 50°C and at 90°C followed by an exotherm at a lower temperature than expected, when compared to the other phospholene oxides. All the exotherms are of approximately equal size when compared to the quantity of sample present.

Despite the initial visual differences in traces between sealed sample pans and perforated sample pans, there is still the evidence of decomposition occurring between 50°C — 100°C and 100°C – 200°C in the form of the endotherms present and onset of the exotherms.

SCAN PARAMETERS

Mettler Power Compensator DSC with TC10A Processor

An atmosphere of static air was chosen to mimic the actual conditions applicable to the making of the foam.

Reference Pan : Empty pan perforated with one hole.

Sample Pan : Experiments performed with both sealed pans and with pans perforated in the lid with one hole.

Start Temperature °C :	25	End Temperature °C :	250
Range FS mW :	50	Offset % :	80
Rate °C min^{-1} :	5	Pan Type 1/2 :	1
Time Iso min :	0	Limit mW :	0
Dyn/Iso 1/2 :	0		

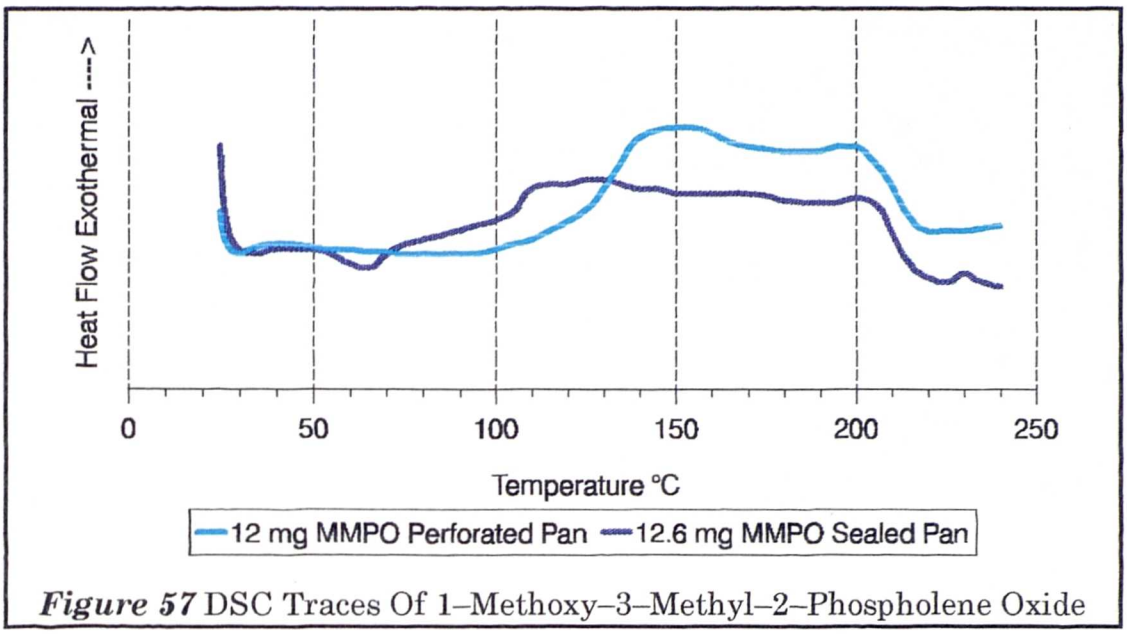


Figure 57 DSC Traces Of 1–Methoxy–3–Methyl–2–Phospholene Oxide

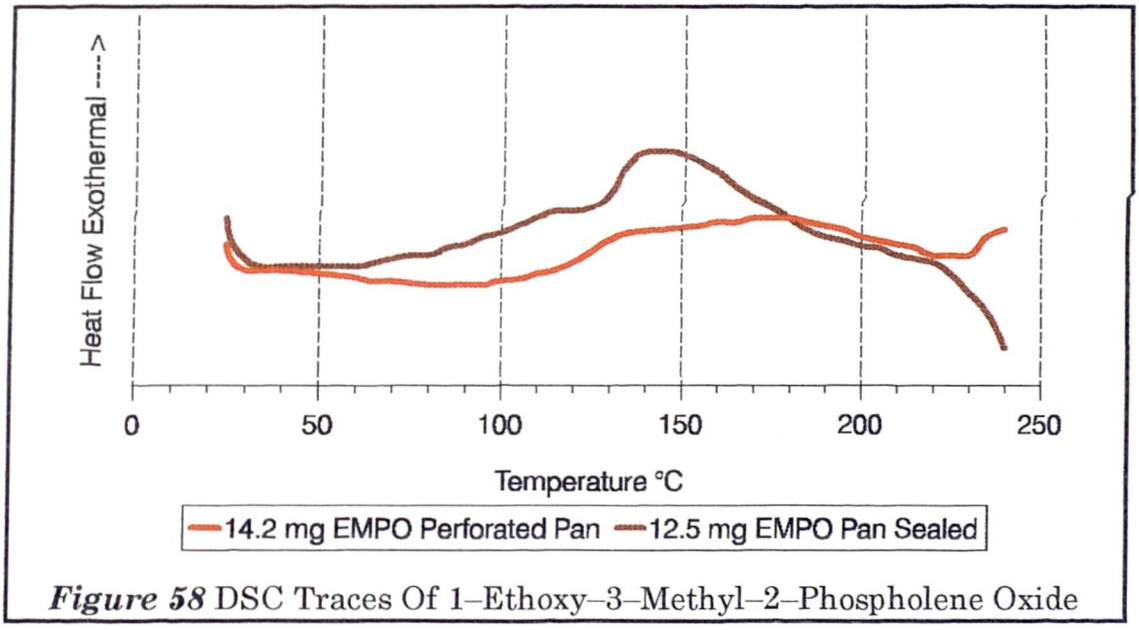


Figure 58 DSC Traces Of 1–Ethoxy–3–Methyl–2–Phospholene Oxide

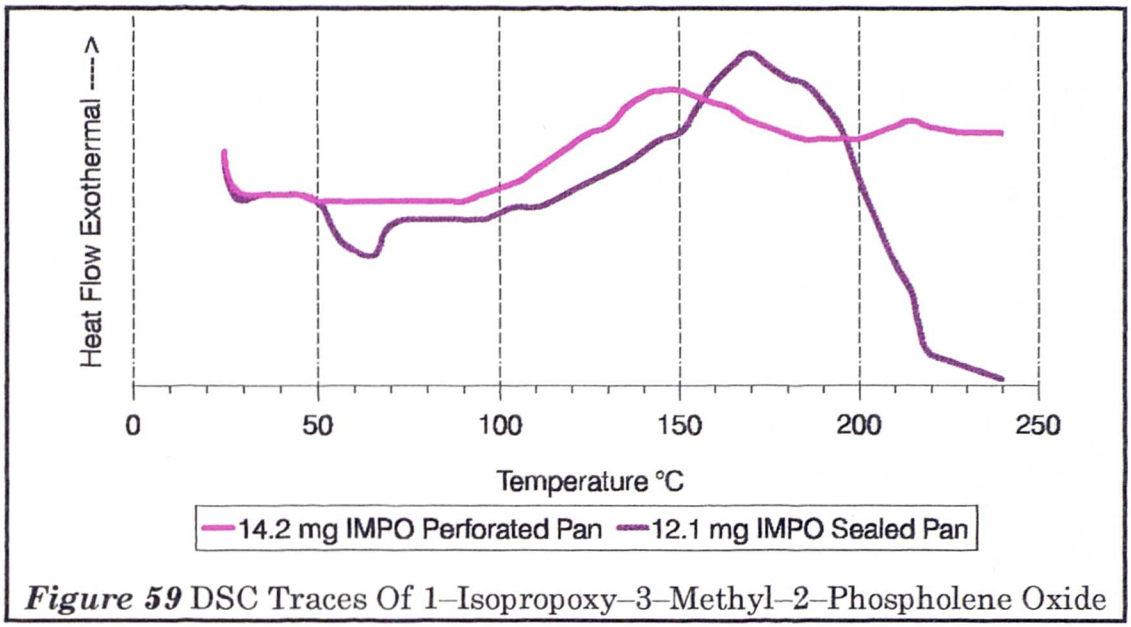


Figure 59 DSC Traces Of 1–Isopropoxy–3–Methyl–2–Phospholene Oxide

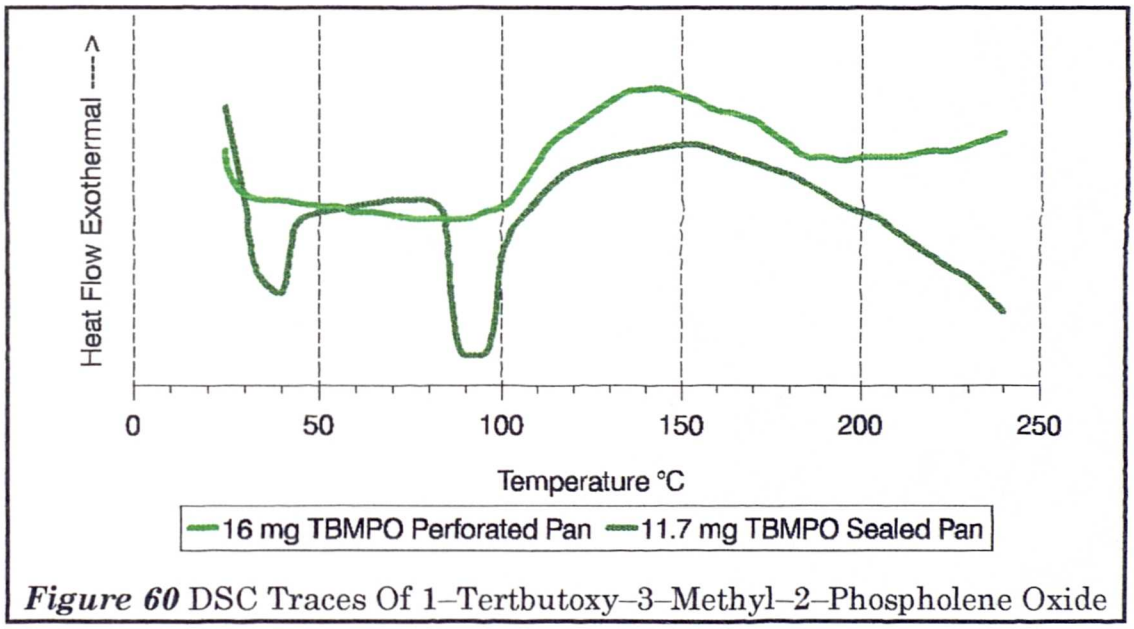


Figure 60 DSC Traces Of 1–Tertbutoxy–3–Methyl–2–Phospholene Oxide

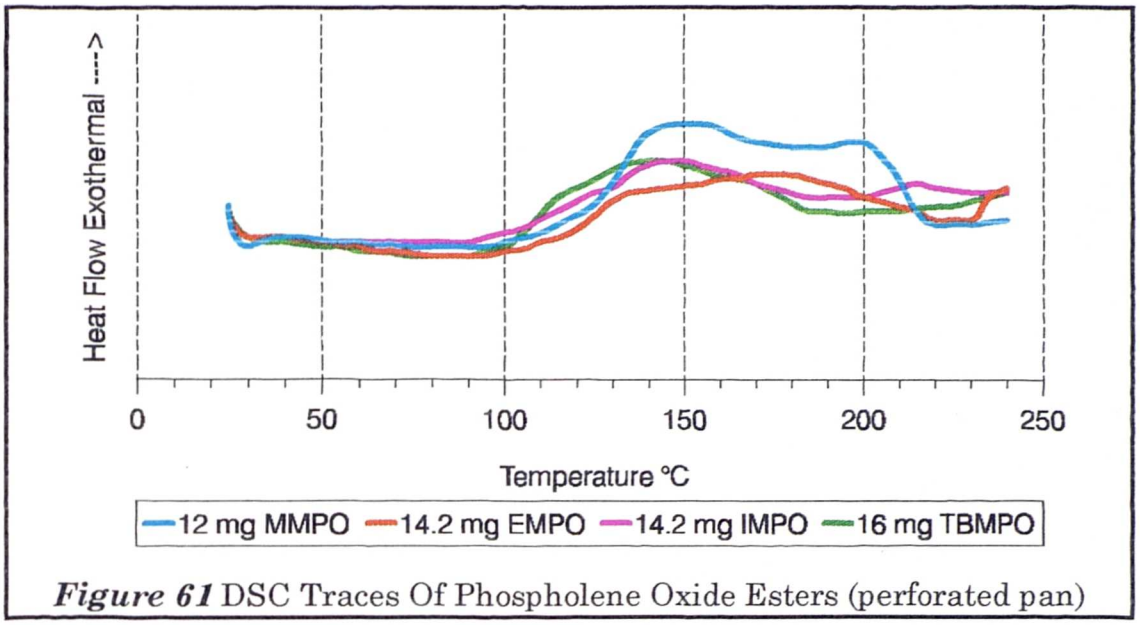


Figure 61 DSC Traces Of Phospholene Oxide Esters (perforated pan)

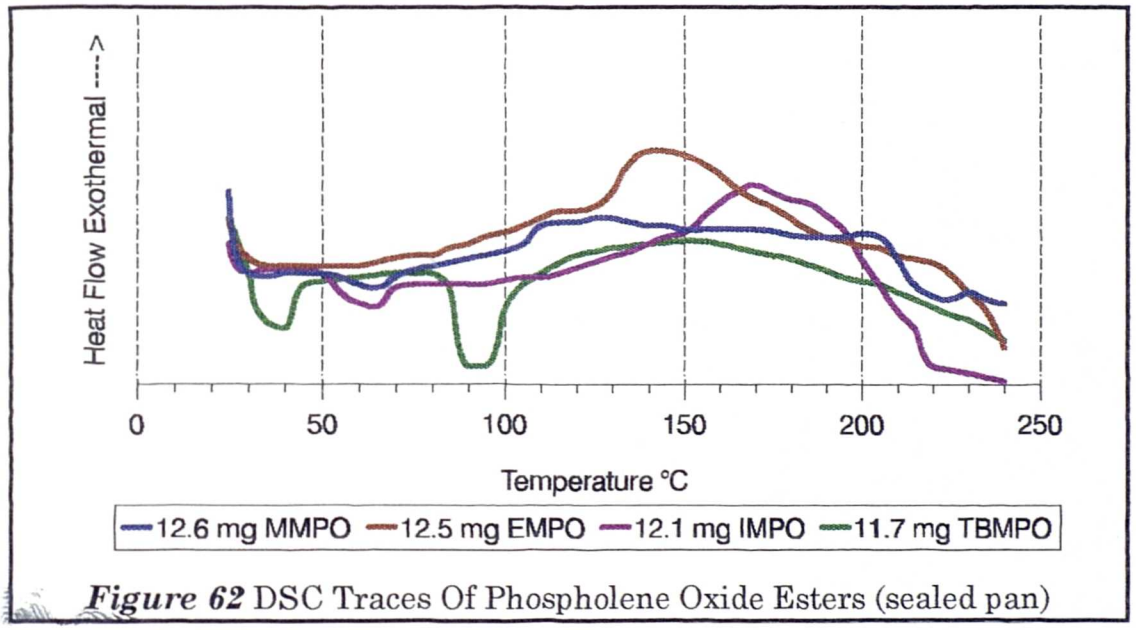


Figure 62 DSC Traces Of Phospholene Oxide Esters (sealed pan)

6.1 Alternative Synthesis Route For Stage II

A new approach to synthesising the target phospholene oxide esters was also investigated. This method involved the direct addition of the alcohol to solid 1,1,1–trichloro–3–methyl–3–phospholene under nitrogen, followed by neutralisation and extraction as before. However this resulted in a violent and extremely vigorous exothermic reaction, which could be explosive when performed with larger quantities. When 10mls of methanol was added to 10 grams of 1,1,1–trichloro–-3–methyl–3 phospholene, the temperature rose to 65°C immediately (i.e. the methanol boiled). After neutralisation with 350mls of aq. $NaHCO_3$ solution and extraction with methylene chloride (4x100mls), the yield was 45%. When 40mls of methanol was added, the yield was still only 47% and the reaction was even more violent. The previous optimised synthesis route was therefore much better, both in yield and safety.

6.2 Trans–Esterification Of MMPO

Trans–esterification experiments were carried out in an attempt to synthesise a phospholene oxide ester with a higher molecular weight and hence greater thermal stability and still retain a high phosphorus content. The anticipated products are shown in Figure 63 overleaf.

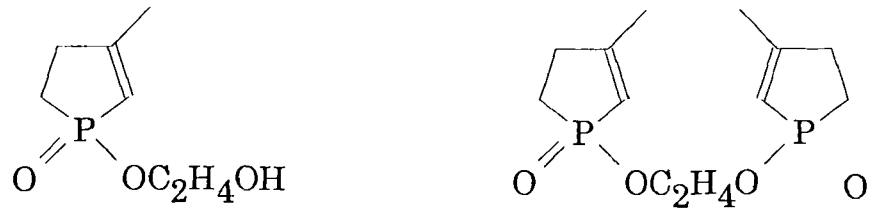


Figure 63 Anticipated Products Of Trans–Esterification Of 1–Methoxy–3–Methyl–2–Phospholene Oxide

On a small scale trans–esterification of 1–methoxy–3–methyl–2–phospholene oxide with ethanediol was attempted. Using Chemometric techniques to generate an experimental design, a full factorial of eight experiments was set up investigating three variables and their effects on the products as shown in Table 6.1. The variables were temperature of reaction 40°C and 80°C, molar ratio of 1–methoxy–3–methyl–2–phospholene oxide : ethanediol, 1:1 and 2:1 and time of reaction 1 hour and 4 hours.

Table 6.1 Full Factorial Analysis Of Trans–Esterification Experiments

Treatment Combination	Temperature	Molar Ratio	Reaction Time	Response
(1)	40°C	1:1	1hr	n/a
a	80°C	1:1	1hr	n/a
b	40°C	2:1	1hr	n/a
ab	80°C	2:1	1hr	n/a
c	40°C	1:1	4hrs	n/a
ac	80°C	1:1	4hrs	n/a
bc	40°C	2:1	4hrs	n/a
abc	80°C	2:1	4hrs	n/a

The response measured was to be the mixture of products, but subsequent analysis of the reaction mixture implied that no reaction had occurred. Analysis of the reaction mixture by chemical ionisation mass spectrometry, indicated no such products as those shown in Figure 63. The only detected product was the unchanged 1–methoxy–3–methyl–2–phospholene oxide.

6.3 Influence Of An Electrophile On Stage II Reaction

Since all the previous Stage II reactions investigated have utilised alcohols (nucleophiles), it was decided to observe the effect that a biphillic alcohol (incorporating both an electrophile and a nucleophile in its structure) would have on the reaction. An ideal biphillic alcohol would have been chloroethanol, however this is a very toxic compound and so 1–chloropropanol was used instead. The anticipated product of the reaction was a chlorinated ester of a phospholene oxide i.e. 1–chloropropoxy–3–methyl–2–phospholene oxide. Following analysis via GC/MS, this was indeed what was found. However there were also two other products, one of which contained two chlorines. The three compounds were formed in the ratio 10 : 2 : 1 respectively.

The conditions used in the reaction were identical to those used in previous experiments i.e. 30mls of 1–chloropropanol added slowly over 15 minutes to a solution of 25g 1,1,1–trichloro–3–methyl–3–phospholene in 400mls methylene chloride held at -10°C. The reactants were then stirred at room temperature for a further hour then neutralised with aqueous sodium hydrogen carbonate solution and extracted with methylene chloride. The solvent was removed from the organic layer leaving an orange oil that was shown to contain a mixture of 1–chloropropoxy–3–methyl–2–phospholene oxide and 2 unknown

compounds, one unknown containing two chlorines (indicated by isotope pattern in mass spectrum), by mass spectrometric analysis. The GC/MS analysis was carried out using a Varian 3400 GC combined with a Finigan 4500 MS. The trace obtained from the gas chromatograph is shown in Figure 64 and the mass spectra in the appendix.

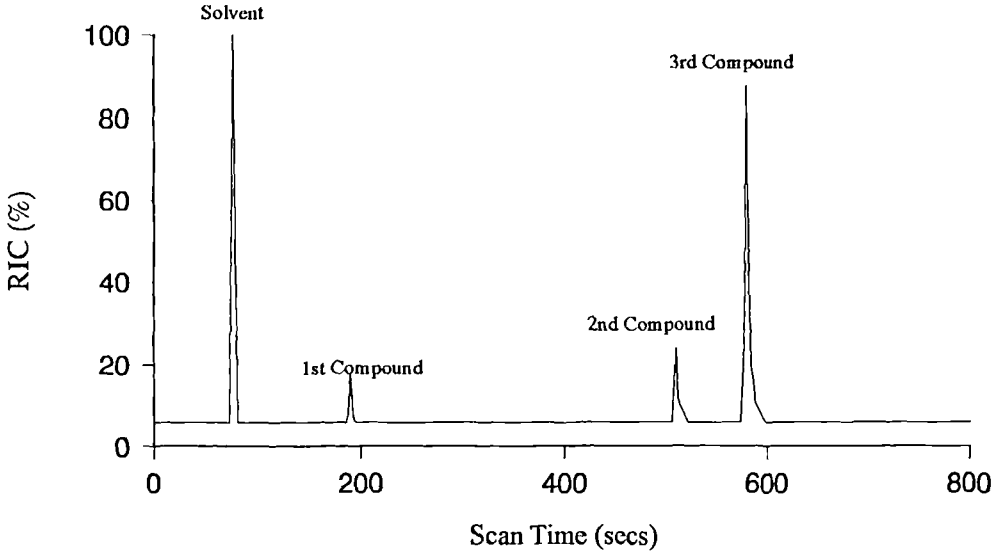
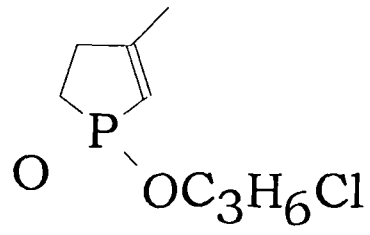


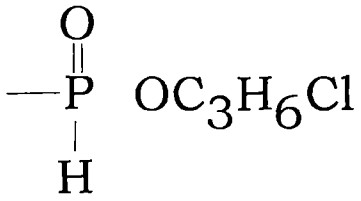
Figure 64 GC Trace From 1–Chloropropanol Reaction

Interpretation of the mass spectra enabled the identification of the most abundant 3rd compound as the target product, i.e. 1–chloropropoxy–3–methyl–2–phospholene oxide.



Molecular Weight 208

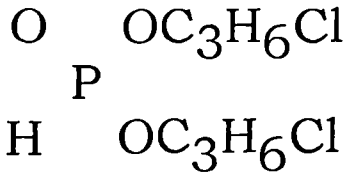
Perusal of the mass spectrum of the 1st compound indicates that it has a molecular weight of 182 and empirical formula $C_6H_{12}O_2PCl$. A possible molecular structure would be :



Molecular Weight 182

This molecule could be formed by the ring structure of 1–chloropropoxy–3–methyl–2–phospholene oxide breaking up at the 3–position.

Preliminary assessment of the mass spectra of the 2nd compound (containing two chlorines) suggested the molecular formula to be :



Molecular Weight 234

This molecule would have to be formed via the break up of the ring system by a 'reverse Diels Alder' reaction. This could result from a decomposition of 1–chloropropoxy–3–methyl–2–phospholene oxide, rather than directly from the reactants.

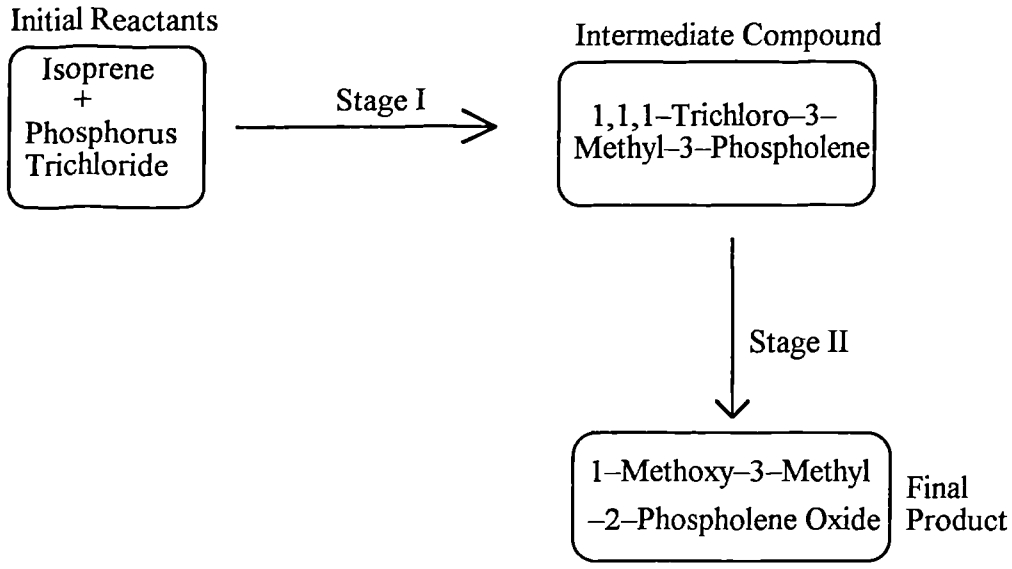
Flame retardant assessment of the impure 1–chloropropoxy–3 –methyl–2–phospholene oxide (b.pt. 175°C), produced as described on page 188, was undertaken by incorporating it at the 16 parts level into a rigid polyurethane foam. The flammability performance was expected to be favourable since the synthesised foam would contain not only phosphorus but also a halogen (22.8% Chlorine & 12.0% Phosphorus). The rigid foam produced had a cream time of 30 seconds, gel time of 72 seconds, rise time of 99 seconds and a set time of 110 seconds, all of which

were substantially higher than those of the other foams synthesised. Also the foam had a rather low density of 23.42 kg m^{-3} (lower than all the previous foams synthesised except the foams loaded with TBMPO see section 5.4). The foam received a B2 Classification in the standard DIN 4102 flame test and had an LOI of 22.6%. Further investigation of the use of electrophiles in the reaction is required to fully assess their influence on the reaction and the products of the reaction. What has been indicated is that for this particular reaction, electrophiles behave in a different manner to nucleophiles.

6.4 Kinetic Investigations Of The Stage Two Reaction

In order to gain insight into the reaction mechanism and Chemometric optimisation results of the Stage II reaction, a kinetic study of Stage II was undertaken. The Stage I reaction mechanism is generally accepted to be a standard 1,4–cycloaddition (a modified Diels Alder reaction). Since the Stage I reaction is extremely air sensitive and uses a highly corrosive reactant, it was decided not to investigate the kinetics of this reaction.

Synthesis Involved For Both Stages Of The Reaction



From the optimisation information obtained in the multivariate analysis, the kinetics of the Stage II reaction appeared far more challenging and interesting. The exact type of nucleophilic addition reaction mechanism was not known and had not been the subject of any previous analysis. By studying the kinetics of the Stage II reaction using standardised techniques [Bamford, C.H. 1965], information on the mechanism could be obtained. Following the decrease in concentration of

1,1,1–trichloro–3–methyl–3–phospholene (TCMP) would be the easiest way to ascertain the rate of the Stage II reaction. The normal method used to follow the change in concentration of a compound is via ultra violet spectroscopy, with both the decrease in reactant and formation of product being monitored, provided that their corresponding absorbance spectra do not overlap.

Figure 65 shows the ultra violet spectrum of the reactant 1,1,1–trichloro–3–methyl–3–phospholene (TCMP). As can be seen it has an intense spectrum, absorbing over the range 200 nm—800 nm (λ_{max} 314 nm). Very dilute solutions of TCMP are needed to obtain a usable spectrum. Using a 2 ml aliquot taken from a stock solution of 0.21g of TCMP in 100 mls of methylene chloride proved adequate.

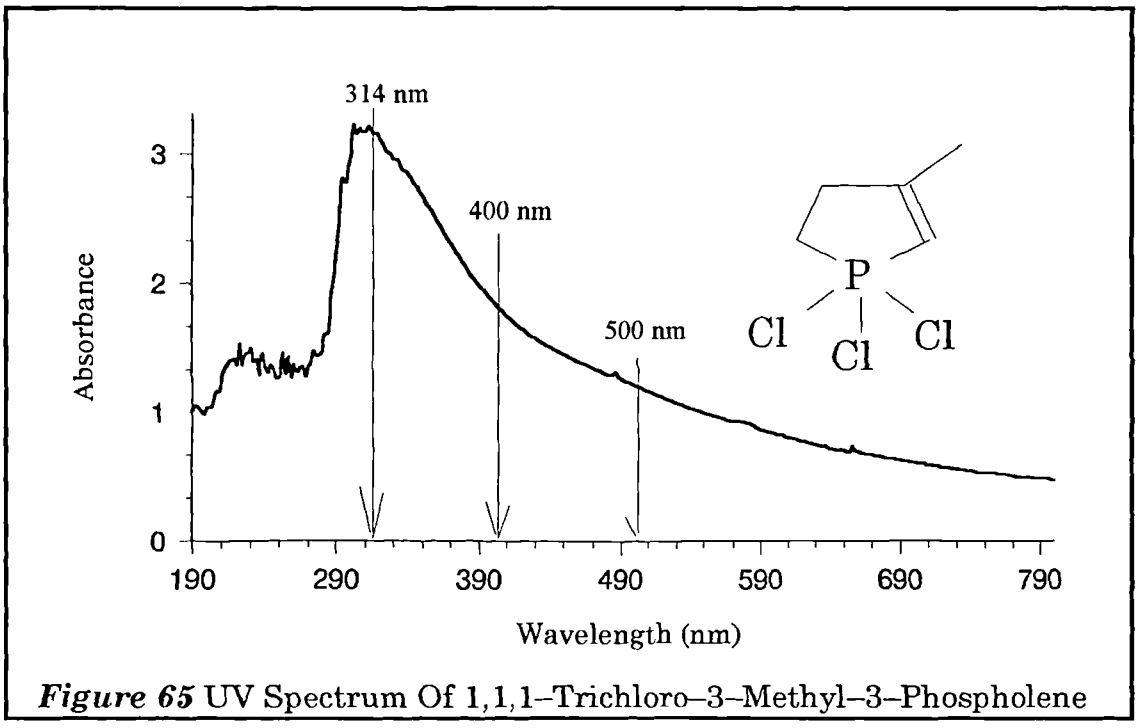


Figure 65 UV Spectrum Of 1,1,1–Trichloro–3–Methyl–3–Phospholene

Figure 66 shows the ultra violet spectrum of the product 1–methoxy–3–methyl–2–phospholene oxide (MMPO). It has a much narrower spectrum, absorbing over the range 200 nm—380 nm (λ_{max} 240

nm). Again a 2 ml aliquot from a stock solution of 0.5g of MMPO in 200 mls of methylene chloride provided a suitable spectrum.

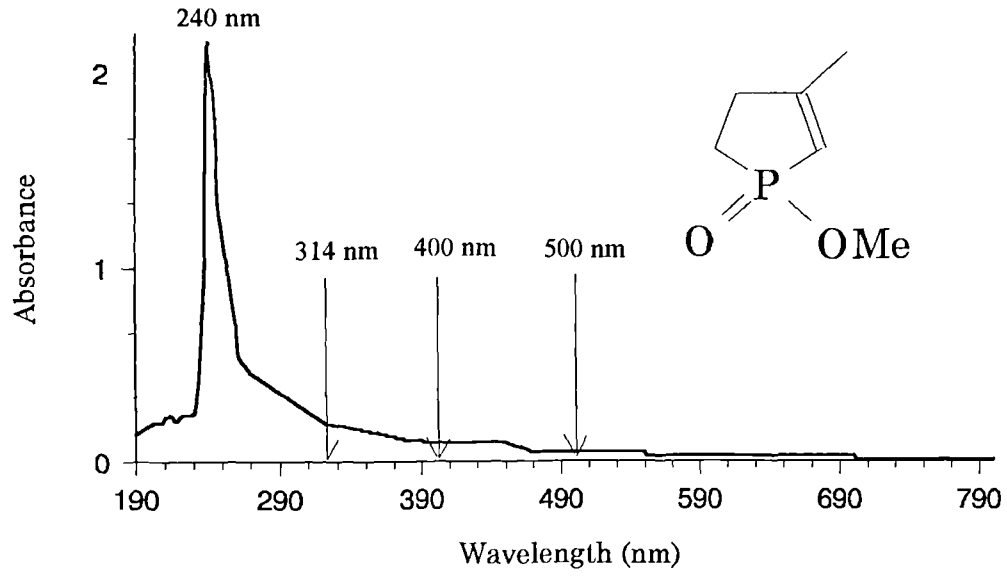


Figure 66 UV Spectrum Of 1–Methoxy–3–Methyl–2–Phospholene Oxide

From the results of the Chemometric investigation of this reaction, the ideal reaction conditions were found to be adding methanol to a solution of 1,1,1–trichloro–3–methyl–3–phospholene in methylene chloride at a temperature of -10°C over 15 minutes then raising the temperature to 25°C (room temperature) and stirring for one hour. Therefore in order to investigate the kinetics of the entire Stage II reaction by ultra violet spectroscopy as desired, methanol would have to be syringed into a jacketed cuvette held at -10°C, containing a solution of 1,1,1–trichloro–3–methyl–3–phospholene in methylene chloride. The reaction could then followed for 15 minutes before raising the temperature to 25°C and following the reaction for the remaining one hour. Since only a very small quantity of reactants were being used, the need for constant stirring could be overlooked, as the initial injection of methanol would hopefully insure adequate mixing. To avoid condensation problems on the

quartz cuvette windows and exclude air from the cuvette the whole volume of the spectrometer sample cell region was subjected to a vigorously flowing blanket of dry argon. Argon was used in place of the nitrogen normally used, since it is heavier than air and would therefore prevail for much longer without the need for isolating the entire spectrometer from the atmosphere. Thus the reaction kinetics were followed via UV absorbance against time mesurement, absorbance values recorded during the reaction being directly proportional to the concentration of the reactant 1,1,1–trichloro–3–methyl–3–phospholene.

The reaction kinetics were investigated in the following way with the conditions as mentioned previously. A 2 ml aliquot from the stock solution of 0.21g of TCMP in 100 mls of methylene chloride was pipetted into a quartz cuvette under an atmosphere of vigorously flowing argon. Next 0.5 ml of methanol was syringed into the cuvette, this represented a large excess to enable the kinetics of the reaction with respect to TCMP only to be determined i.e. pseudo order conditions with respect to TCMP. In addition to the mixing generated by the initial injection of methanol, the cuvette was also shaken vigorously to further ensure complete mixing. The cuvette was then placed in the UV spectrometer and scans of the entire spectrum were recorded every 90 seconds over the whole reaction time (1 Hr & 15 mins). Figure 67 shows the ultra violet spectrum of the reaction mixture after the reaction had finished. As expected this spectrum absorbs over the wavelength range 200 nm—560 nm (λ_{max} 310 nm) a composite spectrum of both TCMP and MMPO. Blanks of methanol, the solvent methylene chloride and the cuvette were completed to ensure that they were transparent over this wavelength region.

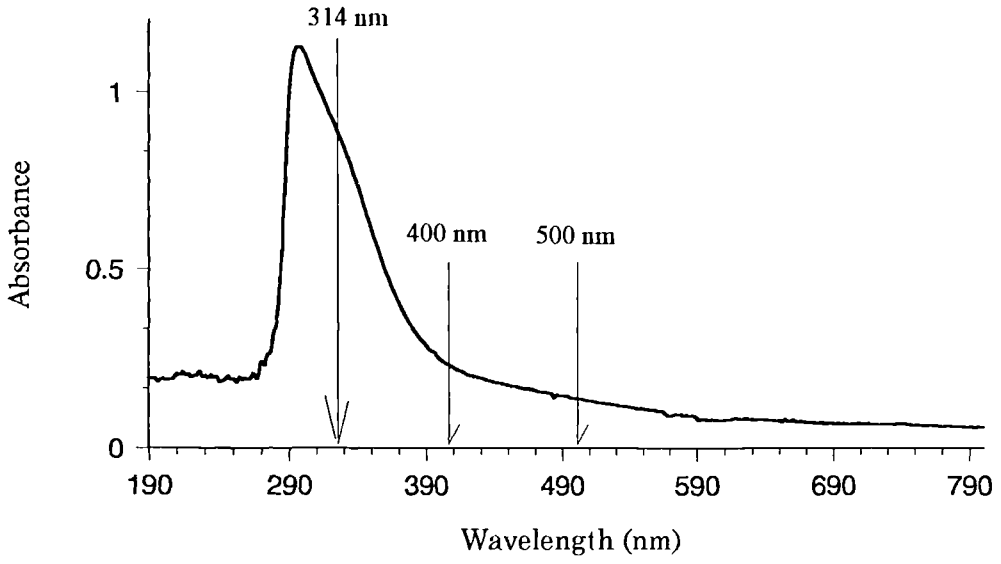


Figure 67 UV Spectrum Of Reaction Mixture After Reaction Completed

Initially the reaction was followed with UV spectrometer by recording an entire spectrum every 90 seconds. This produced the ultra violet spectra seen in Figure 68.

As the reaction proceeds the value for λ_{max} shifts to the left (a lower wavelength) and there is a corresponding drop in the absorbance value as TCMP is consumed. However a discrepancy was observed in these experiments. Before adding the methanol to the TCMP, the absorbance value at 314 nm was 3.18. It was observed that immediately after injecting the methanol and shaking the mixture the absorbance at 314 nm had decreased to 2.5 and there was also an appreciable reduction of colour intensity. Thus it appeared that a very rapid initial reaction had occurred, the evidence being both the absorbance and colour changes. To investigate further it was necessary to scan the reaction over shorter time intervals. To decrease the cycle time (time between scans) from 90 seconds it was necessary to only scan certain wavelengths and not the entire wavelength band because of the limited memory capacity for recorded data of the spectrometer.

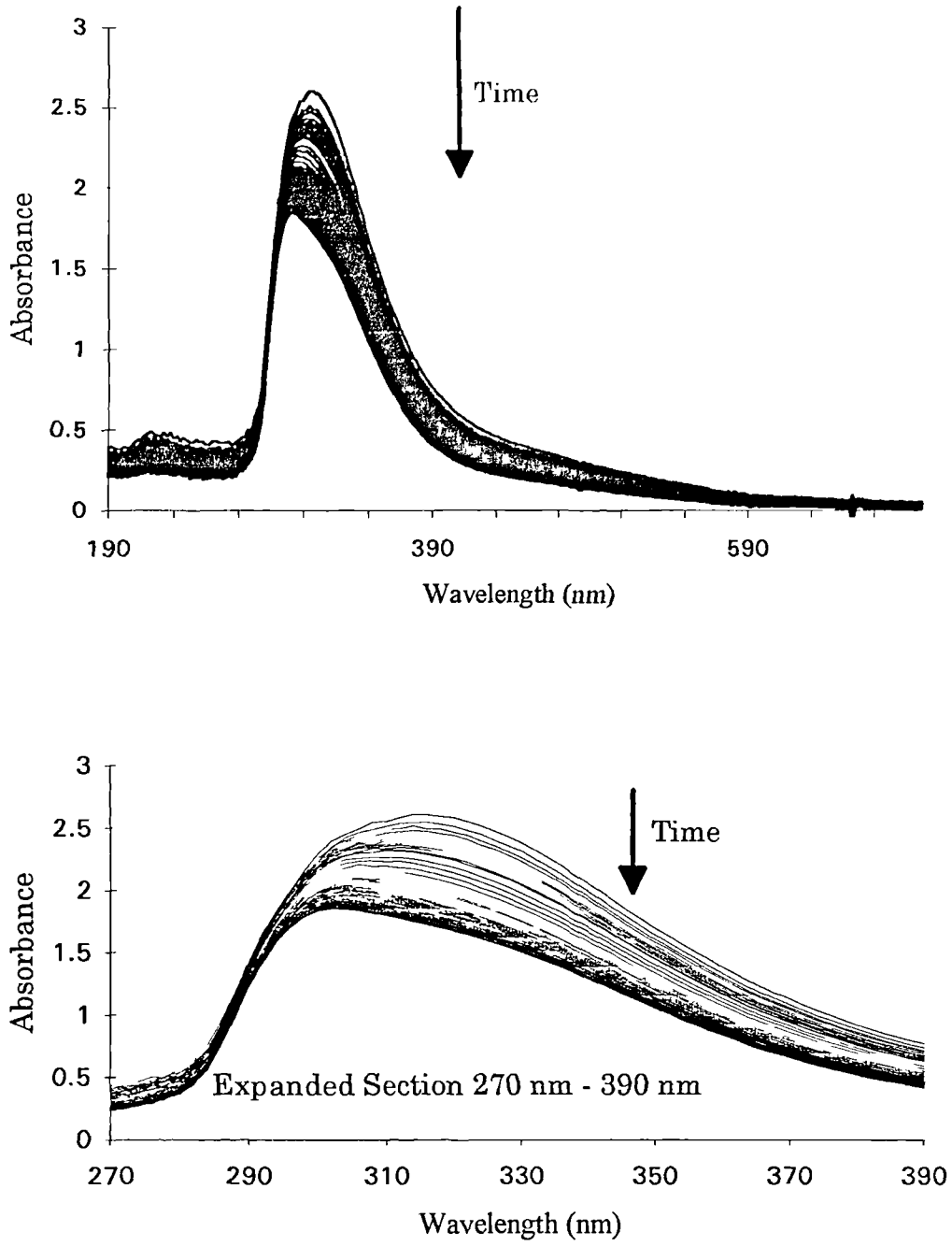


Figure 68 UV Spectra Of Reaction Mixture As Reaction Proceeds

The wavelengths chosen were 314 nm (corresponding to high absorbance values for both TCMP & MMPO), 400 nm & 500 nm (corresponding to absorbance values for TCMP only) and 700 nm & 800 nm (reference background absorbances, that should remain constant at approximately zero). The background absorbances remained constant at values of less than 0.02 and were used to correct all absorbance values by subtracting the respective background absorbance value from the respective absorbance value. Initially the cycle time was reduced to 30 seconds and blank experiments of both TCMP only and methanol only were performed as controls so that effects observed during the experiment were directly attributable to the reaction only. A cuvette containing methylene chloride only was used for the additional blank scan. Figures 69 & 70 show the absorbance change at the wavelengths 314 nm, 400 nm and 500 nm for the entire reaction, that is 15 minutes at -10°C and 1 hour at 25°C (room temperature).

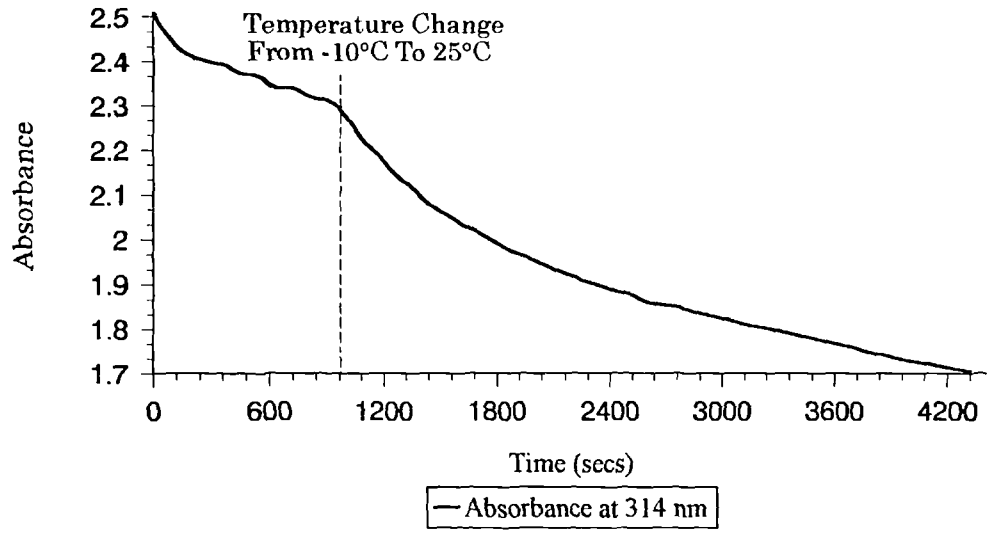


Figure 69 Absorbance Change At 314 nm Over Entire Reaction Time

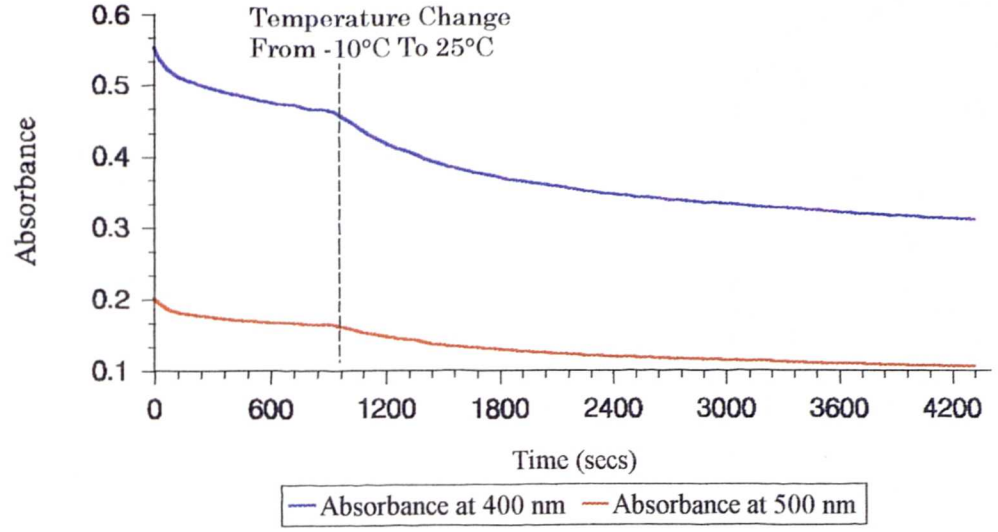


Figure 70 Absorbance Change At 400 nm & 500 nm Over Entire Reaction Time

As can be seen there are two distinct portions to the curve, separated by the temperature change. However there is still the anomaly of the immediate absorbance reduction on mixing. The absorbance values of TCMP before addition of methanol at 400 nm and 500 nm are 1.8 and 1.25 respectively (see Figure 65). Upon addition of the methanol, the first recorded absorbance values at 400 nm and 500 nm are 0.54 and 0.2 (see Figure 70). This absorbance discrepancy is therefore due to an initial rapid reaction that is too fast to be recorded by the spectrometer. Figures 69 and 70 all show the subsequent slower reaction up to 900 seconds (reaction at -10°C) followed by another reaction corresponding to the room temperature stage of the reaction.

It is therefore postulated that the reaction mechanism is not a straight forward addition reaction followed by a subsequent elimination reaction as was first believed, but involves three separate stages. Figures 71 and 72 show the entire reaction at -10°C, Figures 73 and 74 show the entire reaction at 25°C (room temperature), at the 3 chosen wavelengths,

314 nm – absorbance proportional to both reactant and product, 400 nm and 500 nm – absorbencies proportional to concentration of reactant only.

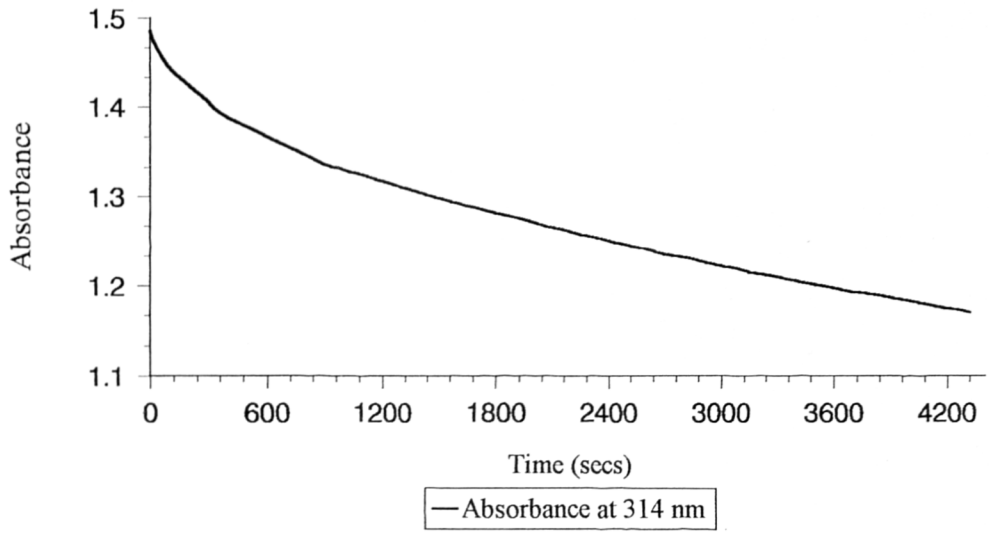


Figure 71 Absorbance Change At 314 nm Over Entire Reaction At -10°C

Each show evidence of this initial rapid reaction and the recorded starting absorbance values are different; for the -10°C reaction, at 314nm the first recorded absorbance value is approximately 1.5, whereas for the room temperature reaction the first recorded absorbance value is approximately 2.4, (for the stock solution of TCMP used in both reactions the recorded absorbance value is approximately 2.8). This infers that the rate of the initial rapid reaction is increased by lowering the temperature.

This was also suggested by the results obtained from the multivariate optimisation process, see section 3.1.

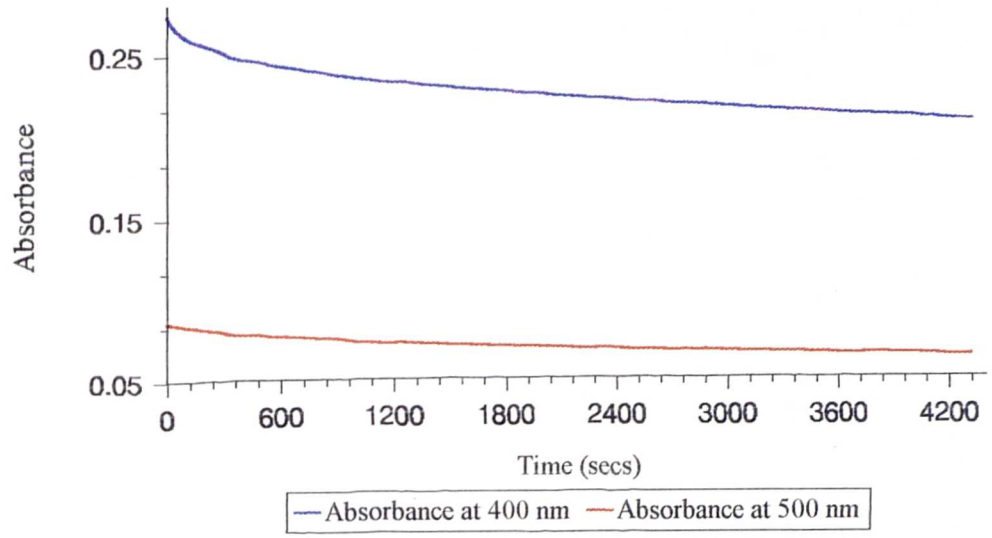


Figure 72 Absorbance Change At 400nm & 500nm Over Entire Reaction At -10°C

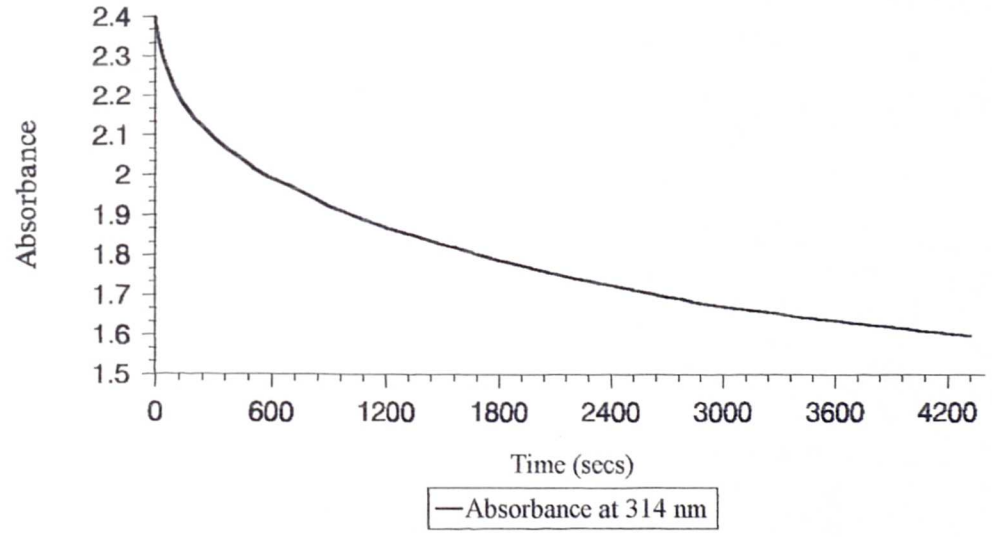


Figure 73 Absorbance Change At 314 nm Over Entire Reaction At 25°C

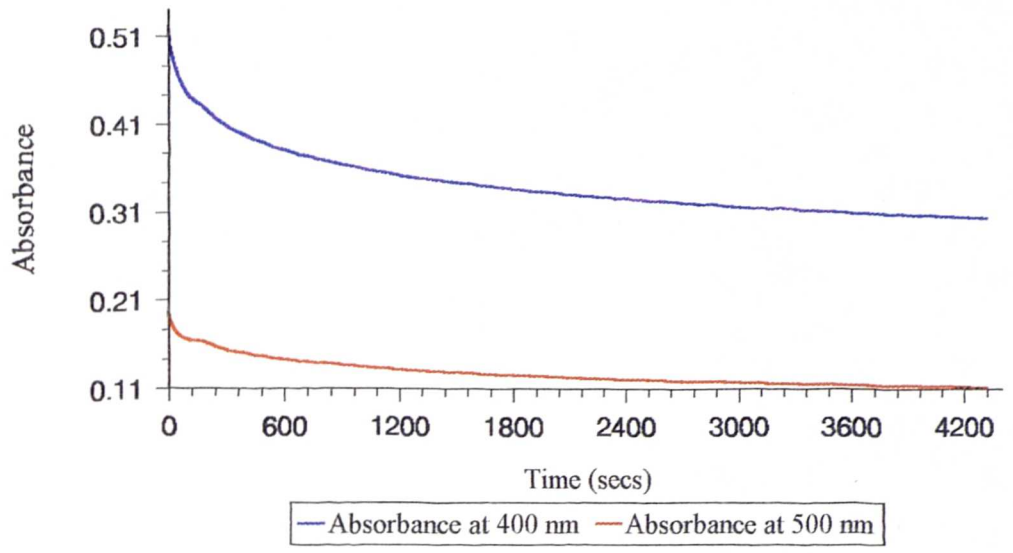


Figure 74 Absorbance Change At 400 nm & 500 nm Over Entire Reaction At 25°C

In order to fully investigate the kinetics, this initial rapid reaction needed to be investigated. To this end, the initial 15 minute stage was investigated at various the temperatures. Figure 75 shows the kinetic traces obtained at 400 nm (reactant absorption)for this reaction stage performed at 25°C, 4°C, 1°C, -5°C and -10°C. The absorbance values decrease as the temperature is reduced. The initial very steep portion of each of the curves, can be clearly seen and is more evident at the lowest temperature, this may be attributable to the end of an initial fast reaction.

Since an excess of methanol is present the reaction after this initial rapid reaction might be expected to be a pseudo first order reaction with respect to the concentration of the reactant TCMP. Figure 76 shows the graphs of a 1^{st} order plot and a 2^{nd} order plot for the reaction at -10°C, assuming that the reaction is complete at an absorbance value of 0.47, i.e. assuming $Ln[reactant] \propto Ln[A_t - A_\infty]$ where A_t is the absorbance at time t and A_∞ is the absorbance at reaction completion, A_∞=0.47 in this case.

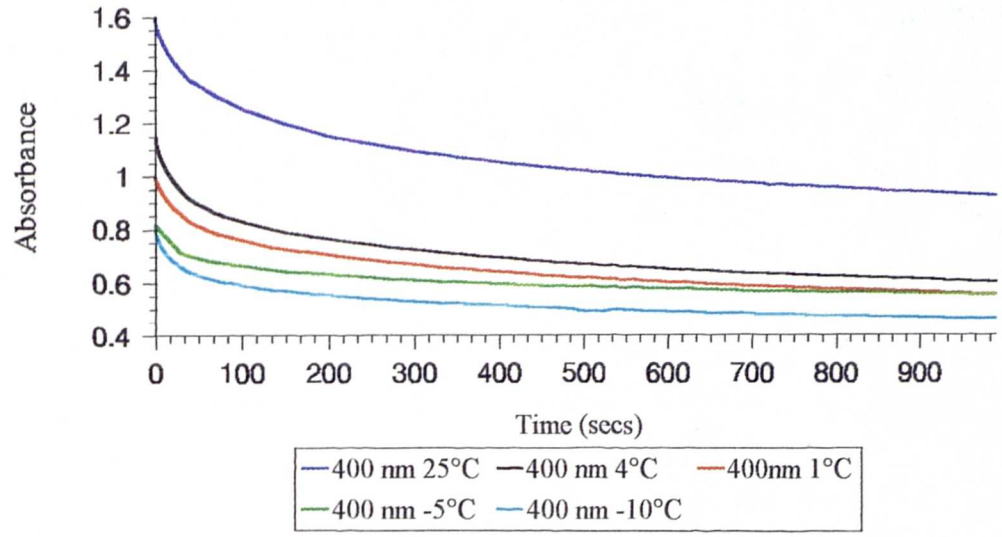


Figure 75 Absorbance Change At 400 nm For First 15 Minutes Of Reaction At Various Temperatures

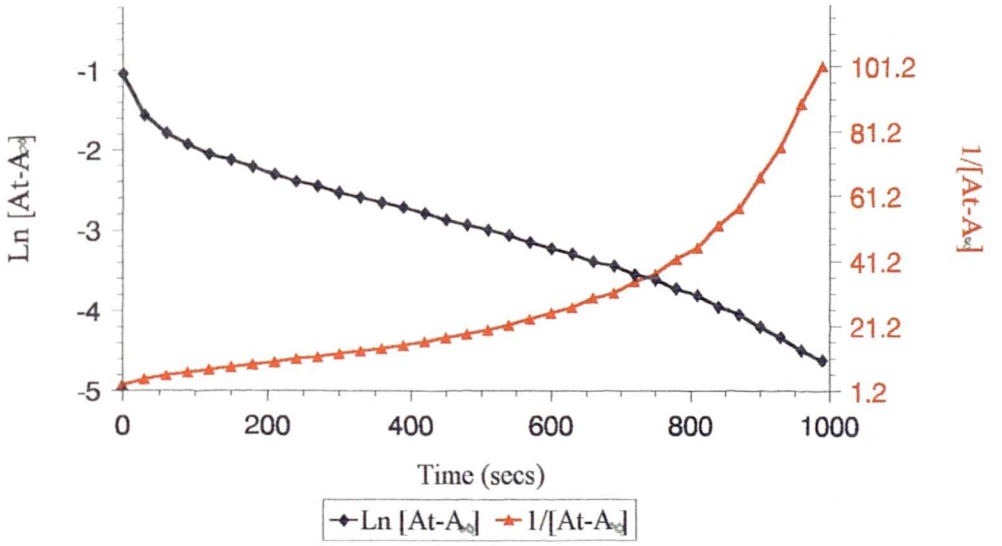


Figure 76 First Order Plot At -10°C Of Absorbance Values At 400 nm

Second Order Plot At -10°C Of Absorbance Values At 400 nm

Neither of the plots is a straight line, even if the initial steep portion of the original curve (the first few data points) is ignored. This behaviour was also shown at all the other temperatures investigated (25°C, 4°C, 1°C and -5°C see Figure 75). Until the kinetics of the initial rapid reaction have been identified it is impossible to try and ascertain the kinetics of the subsequent stages of the reaction. A calibration plot of concentration of TCMP against absorbance could be used to obtain the concentration of TCMP at various time. However this calibration plot might prove to be a false indication of the concentration of TCMP. This would be the case if, during the initial rapid reaction, a further unknown intermediate which absorbs over the same wavelength range as TCMP is generated. It is therefore better to first identify the kinetics of the initial rapid reaction before precceding with any subsequent kinetic interpretation.

6.5 Investigation Of The Initial Rapid Reaction

Preliminary investigation was attempted of the initial rapid reaction by operating the UV spectrometer with its scan time set at its most rapid, namely 0.1 seconds. Methanol was rapidly injected from a syringe into a cuvette containing 1,1,1–Trichloro–3–Methyl –3–Phospholene (TCMP) and held at -10°C. As shown by the kinetic traces in Figure 77, these experiments failed to provide suitable data for kinetic analysis. This was mainly because the mixing time achieved was approximately 1-2 seconds during which time the rapid reaction had occurred to a significant extent.

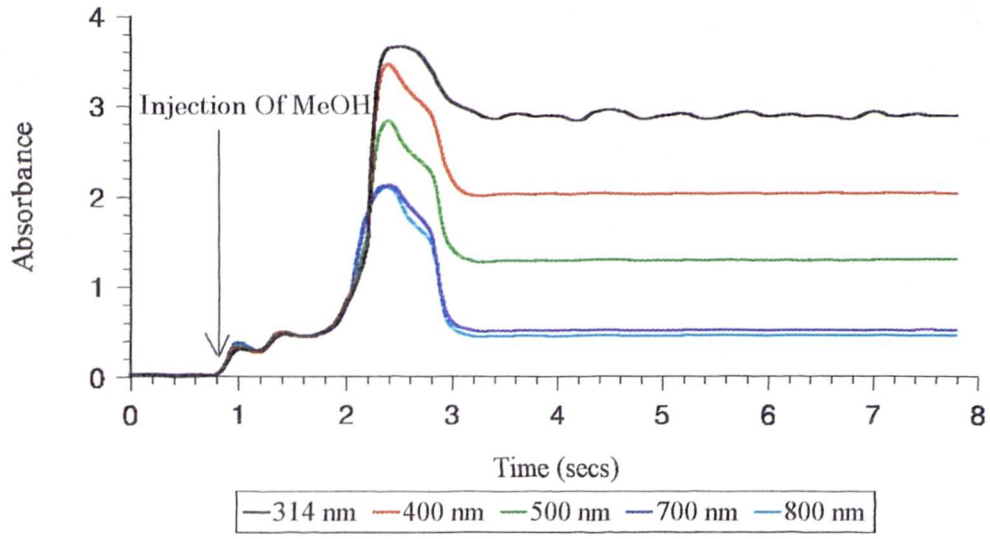


Figure 77 Preliminary Attempt To Follow Initial Rapid Reaction

The turbulence caused by the injection of methanol also caused brief errors in the absorbance values recorded as well as increasing the baseline absorbance values at 700 nm and 800 nm from almost zero to 0.25 as can be seen by inspection of Figure 77.

A 'Y shaped' mixer/injection system, constructed to fit into the cuvette, was used to decrease the mixing time of the two solutions. The design is illustrated in Figure 78. The cuvette was also held at 25°C instead of -10°C in order to slow down the rate of the initial rapid reaction. The results obtained from these experiments are also shown in Figure 78 and indicate that the mixing time did not decrease to any extent and the baseline shift still occurred.

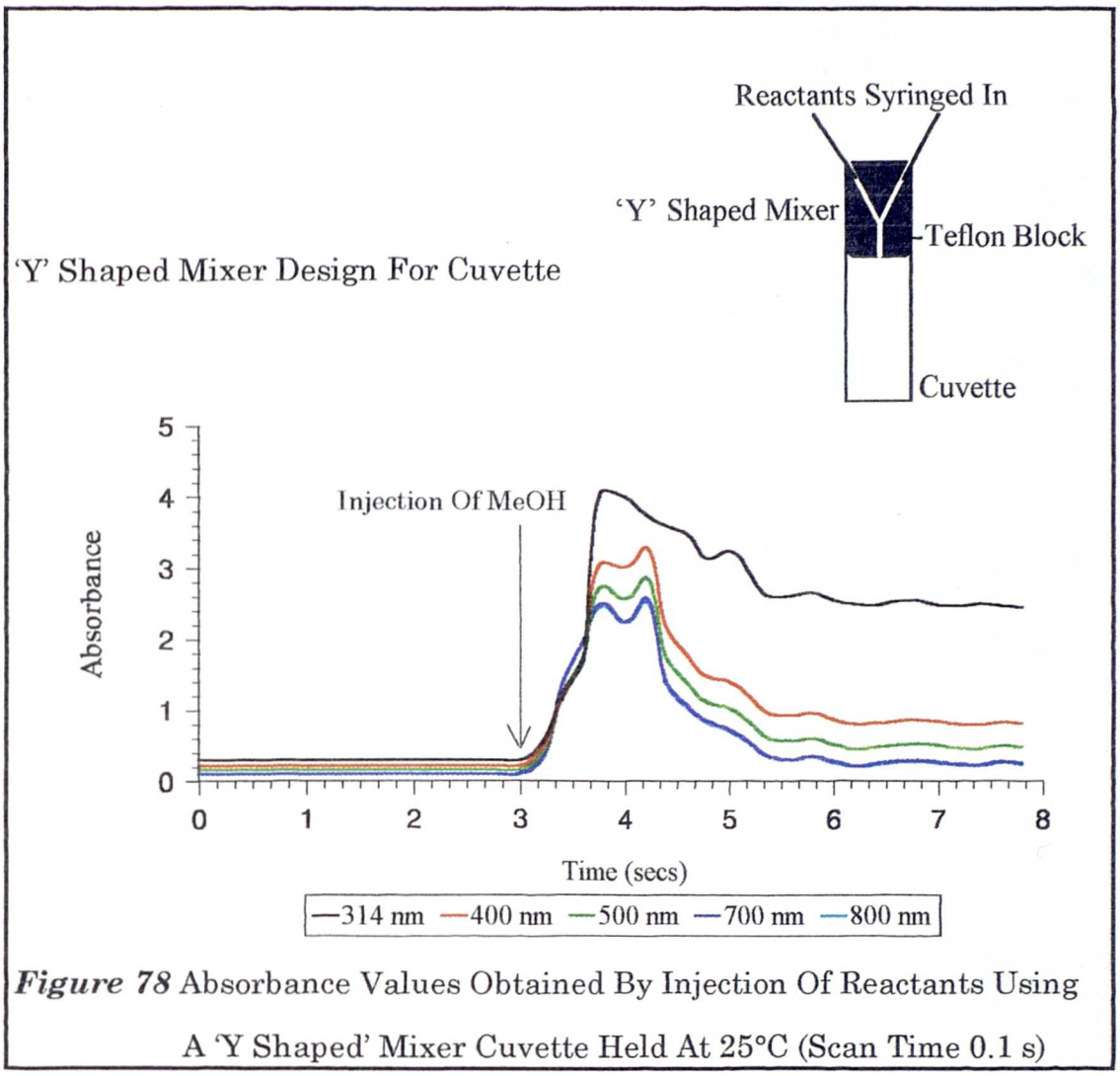


Figure 78 Absorbance Values Obtained By Injection Of Reactants Using A 'Y Shaped' Mixer Cuvette Held At 25°C (Scan Time 0.1 s)

A final attempt to monitor the rapid reaction in the spectrometer was made utilising a 'T shaped' mixer fitted to a reduced volume cuvette This cuvette design reduced the amount of reactants that needed to be injected and the 'T shaped' design shortens the time between mixing and scanning, since the exit point from the mixer is located in the path of the scan beam. The system design and the results are shown in Figure 79.

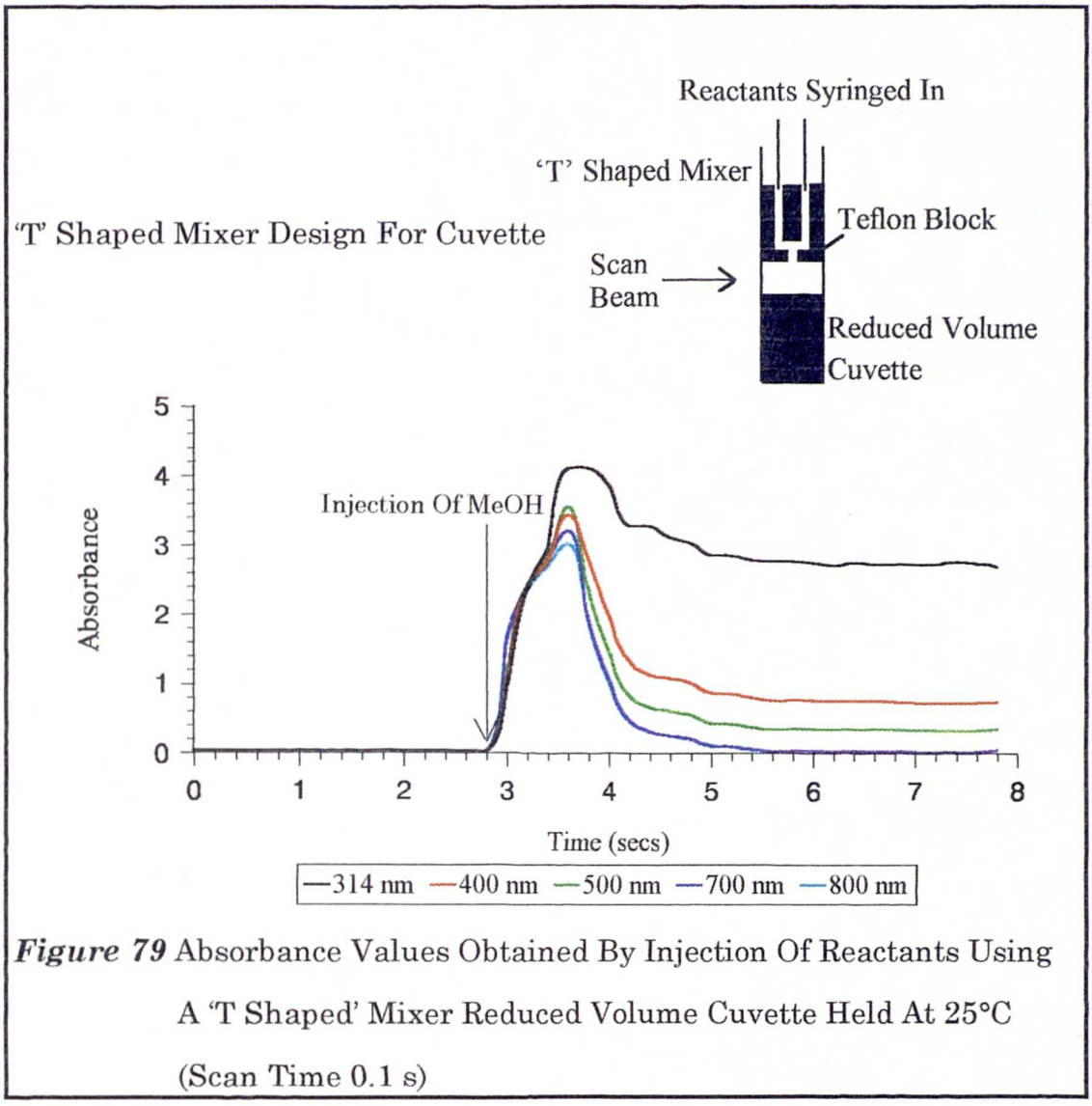


Figure 79 Absorbance Values Obtained By Injection Of Reactants Using A 'T Shaped' Mixer Reduced Volume Cuvette Held At 25°C (Scan Time 0.1 s)

A fifty percent reduction in the mixing time was achieved with the 'T' shaped mixer reduced volume cuvette, but a similar baseline absorbance shift still occurred, making the results useless.

6.6 Experiments With Stop–Flow Kinetics Cell

Since the initial rapid reaction had proved to be too fast to be monitored by repetitive scanning of the conventional UV spectrometer it was decided to switch to the stop–flow technique [Caldin, E.F. 1964] which has been developed to monitor rapid reactions with $t_{1/2}$ in the range

1 ms — 0.1 s. The speed of a reaction which can be followed by conventional means is limited by the error involved in the time taken to mix the components and the thoroughness of that mixing. In this rapid mixing technique, the reactants are mixed continuously in a flow system until mixing is suddenly stopped (hence the name "Stop–Flow Kinetics"). At this point the system ceases to be in dynamic equilibrium and the rate of reaction can be followed photometrically at a chosen wavelength by means of a monochromator. The very fast data acquisition times are possible only with the aid of an interfaced computer and relevant software, enabling digitised data recording over a set time period.

The stop–flow equipment used is shown in Figure 80. The experimental apparatus consists of two syringes connected to two way valves. The valves are used to draw in fresh solutions, one reagent to each syringe, then by changing the valve position, to inject the double stream through a mixing cell and out into a waste collector. The mixing cell has quartz windows orthogonal to the mixing streams through which light can be passed to monitor the reaction. The light is fed to the cell by optic fibres which also pass the transmitted light through to a monochromator to a photomultiplier tube to measure the intensity of the light at the selected wavelength. The output signal (v), which is directly proportional to the intensity of light falling on the photomultiplier, is fed via an amplifier to the computerised data acquisition system. Being a single beam system and therefore having no reference beam, a means of measuring light off and light on readings is needed so that light intensity can be converted into absorbance values. This is provided by a shutter mounted on the photomultiplier tube housing.

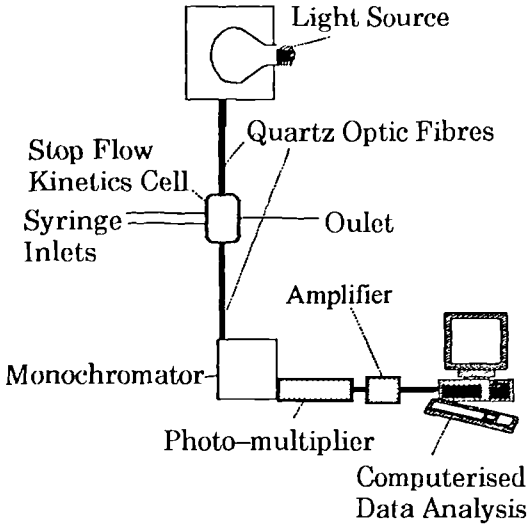


Figure 80 Experimental Set Up Of Stop–Flow Kinetics Cell

The monochromator is therefore set at one chosen characteristic wavelength for the specific reaction and the reactants are injected into the specially designed Teflon flow cell.

The output data is displayed graphically on the computer screen as voltage against time in real time as the reaction proceeds. Before each experiment the photo-multiplier is calibrated to give an output of approximately 1 volt, with no sample in the flow cell (maximum intensity of incident light – shutter open) and an output of approximately zero volts with no incident light (shutter closed). The relationship between light intensity and voltage is a linear proportionality.

Using the Beer-Lambert law :

$$I_i = I_0 e^{-\alpha[c]l}$$

$$\therefore -\mathrm{Ln}(I_i / I_0) = \alpha[c]l = \text{absorbance}$$

where I_i = Intensity of light emerging from the sample $\propto$ voltage output from photo-multiplier.

I_0 = Incident intensity of light on sample.

$[c]$ = Concentration of reactant.

α = Naperian absorption coefficient

l = Path length of the flow cell.

Remembering that voltage output (V) from the photo-multiplier is proportional to the intensity, then $I_i = kV_i + C$ and $I_0 = kV_0 + C$ where k = constant of proportionality, C = constant. But the equipment is pre-set so that output voltage is set to zero when the incident light is blocked off with the shutter, that is when $I_0 = 0$ and so $C = 0$ under these circumstances.

$$\therefore -\mathrm{Ln}(kV_i / kV_0) = \alpha[c]l = \text{absorbance}$$

$$\therefore -\mathrm{Ln}(V_i / V_0) = -\mathrm{Ln}(I_i / I_0) = \alpha[c]l = \text{absorbance}$$

Thus a calibration plot of [c] against $\mathrm{Ln}(V_i/V_0)$ can be obtained by determining Vi/Vo ratios for various known concentrations of TCMP. The plot can subsequently be used to interpret kinetic curves of the type shown in Figure 81.

Figure 81, presents a typical raw output data i.e. volts versus time, from a stop flow experimental. This shows the pre–setting of the maximum and minimum light intensities, followed by the rapid injection of the two reactants into the stop–flow cell. A very rapid decrease in the output signal, i.e. a rapid decrease in the concentration of the reactant 1,1,1–trichloro–3–methyl–3–phospholene is then observed.

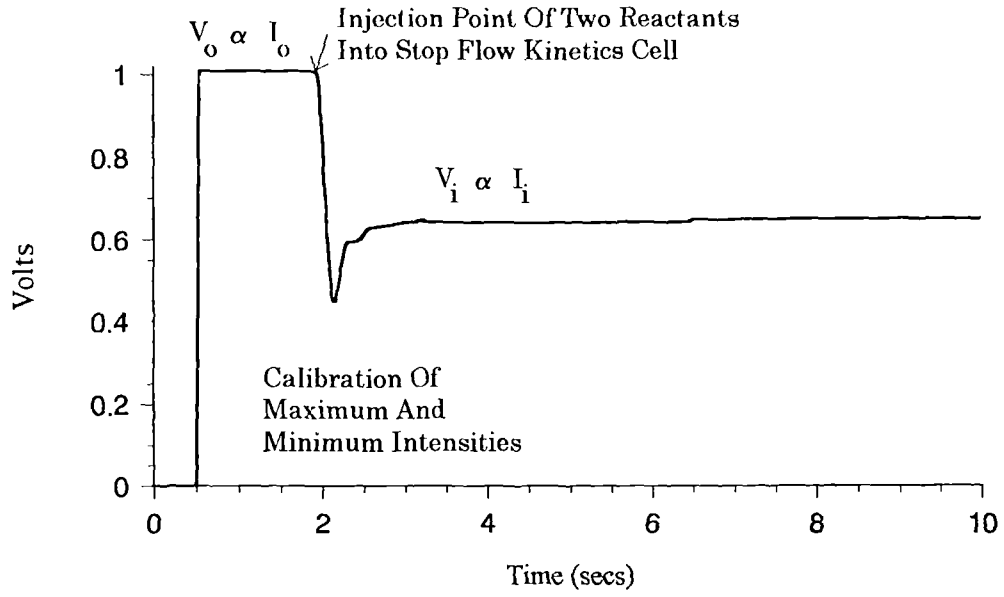
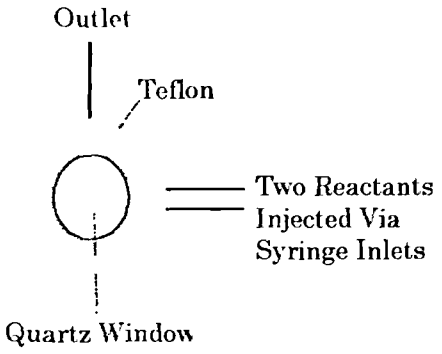


Figure 81 Output Signal Obtained From Stop–Flow Kinetics Cell Set Up

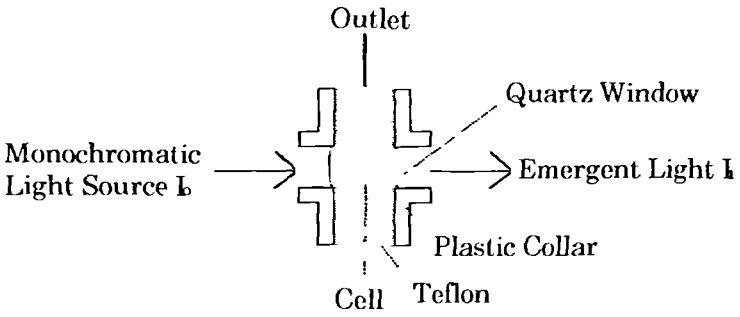
As a preliminary, mixing time experiments were conducted on this cell to ascertain the speed and thoroughness of mixing. A solution of an acid (0.1 M HCl), indicator (phenolphthalein) and base (0.1 M NaOH), 'one drop of base away' from neutralisation was prepared and drawn into one of the syringes. The second syringe contained the base (0.1 M NaOH) previously used. The photomultiplier was calibrated and then the computer set to record data over a period of time. During this recording session the contents of the two syringes were simultaneously injected through the mixing cell. A dramatic change in absorbance due to the

colour change, was detected upon neutralisation of the acid/base solution by further base in approximately 1 ms. This meant that the two solutions were mixed in approximately 1 ms and thus demonstrated that the mixing and recording capabilities of the apparatus set up were commensurate with the task required of them.

A 'stop–flow kinetics' cell was especially designed for this work and is shown in Figure 82.



Front View Of Stop–Flow Kinetics Cell



Side View Of Stop–Flow Kinetics Cell

Figure 82 Stop–Flow Kinetics Cell

Because the photomultiplier was only sensitive at wavelengths above 450 nm, the monochromator was set at 500 nm for the initial studies of the fast reaction of the Stage II reaction. At this wavelength

only the reactant, 1,1,1–trichloro–3–methyl–3–phospholene, absorbs and so no interference from 1–methoxy–3–methyl–2–phospholene oxide, the product, would occur. Therefore the absorbance change at 500 nm is attributable to the change in concentration of 1,1,1–trichloro–3–methyl–3–phospholene alone.

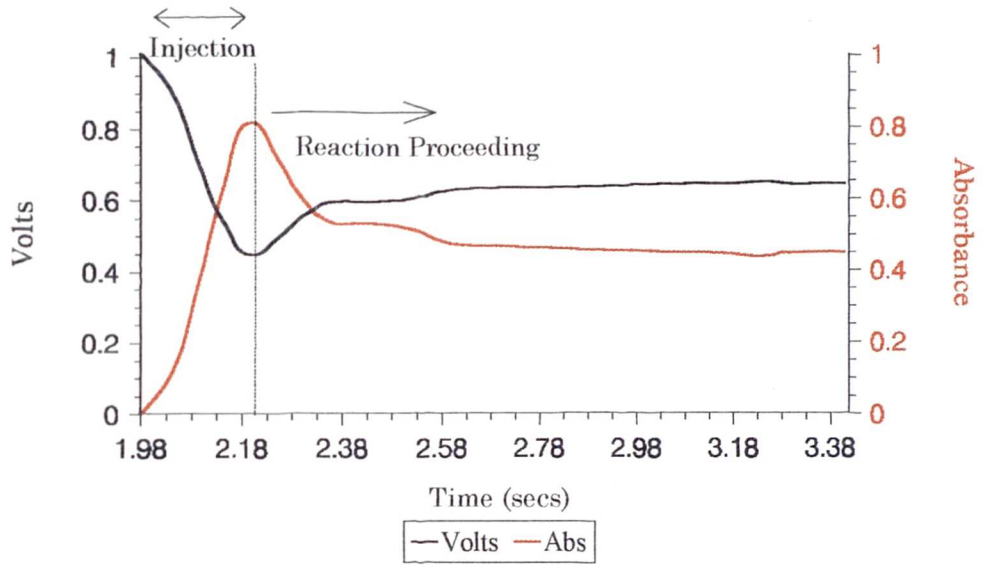


Figure 83 Stop–Flow Kinetic Data For Stage II Reaction

Figure 83 shows the reactant decay curve on an expanded time scale compared to that for Figure 81. The photomultiplier output, shown in volts, is also converted into an absorbance value as detailed on page 210 (absorbance = - $Ln(V_i / V_o)$). Assuming that absorbance is directly proportional to the reactant concentration, then 1st and 2nd order kinetic plots can be obtained by plotting Ln(Absorbance) against time or 1/Absorbance against time. These plots are shown in Figures 84 and 85 respectively. It was subsequently found that the photo-multiplier used was generating a substantial and erratic baseline drift thus effectively creating a systematic random error in each absorbance value recorded.

Any interpretation of the data is therefore impossible. A photo-diode has a very stable baseline signal and so replacing the photo-multiplier with a photo-diode would eliminate the baseline drift problem. In addition to this baseline problem it was also observed that non–uniform mixing between methanol and the 1,1,1–trichloro–3–methyl–3–phospholene in methylene

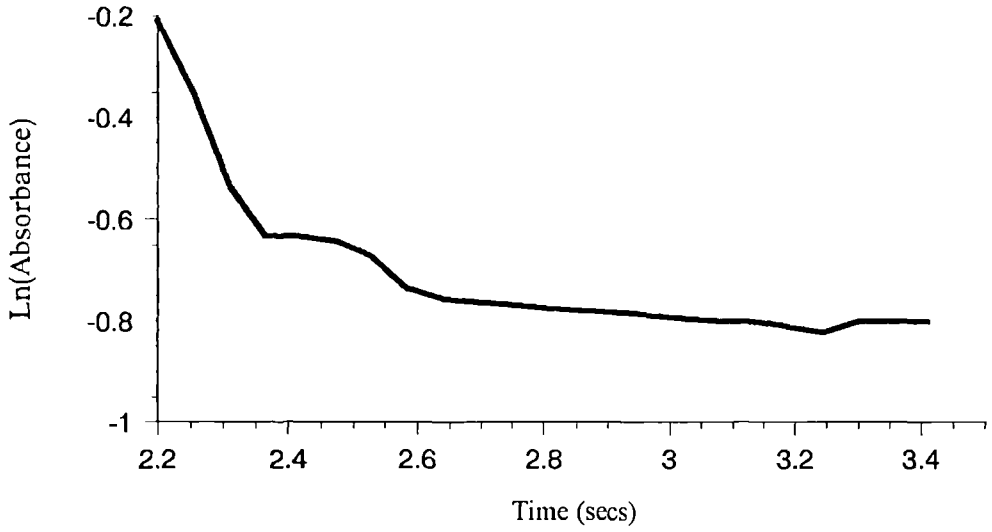


Figure 84 First Order Plot Of Reaction Data From Figure 83

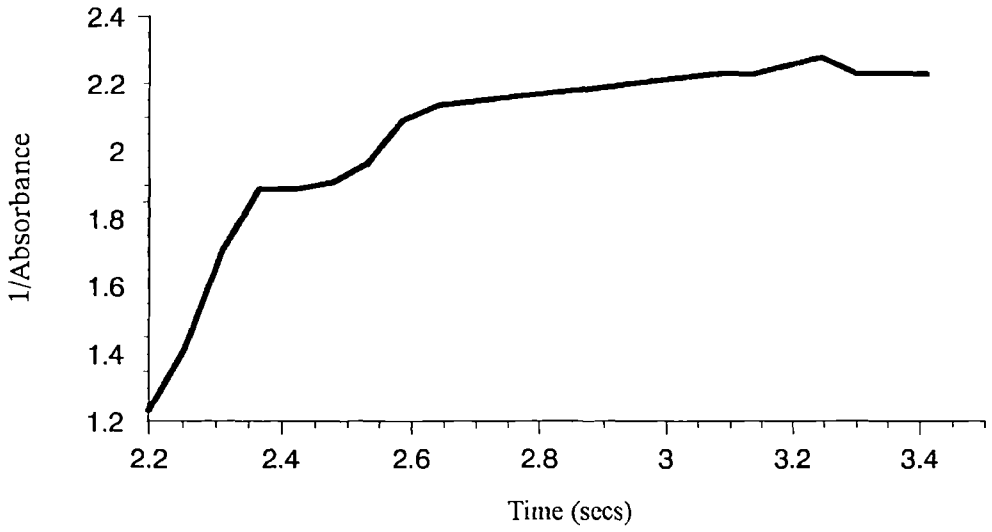


Figure 85 Second Order Plot Of Reaction Data From Figure 83

chloride also creates fluctuations in the absorbance values recorded. The miscibility problem could be overcome by averaging the results from all experiments performed, provided the previously mentioned baseline fluctuation had been minimised.

The photomultiplier used had a response range with a minimum wavelength of 450 nm. A detector responsive at 314 nm would obviously enhance the experimental capability, as for TCMP $\alpha_{314} >> \alpha_{500}$. This would be attainable with a suitable photodiode whose optimum operating wavelength was 314 nm. However due to time running out, it was not possible to design, build and use this alternative apparatus. In hindsight it would have been better initially to have built a dedicated piece of equipment to follow the initial rapid reaction, rather than trying to modify and use the apparatus, an undergraduate teaching experiment, available .

6.7 Conclusions From Experiments With Stop–Flow Kinetics Cell

Although the experiments performed failed to identify the kinetic parameters of the inital rapid reaction, the kinetic curves obtained do indicate that the stop–flow technique has the potential to provide kinetic data on the initial rapid reaction of interest. A more extensive attempt to utilise this approach in the future would appear to be justified. The kinetic data recorded with the UV spectrometer (section 6.3) is valid but the data obtained will only yield information on the entire reaction after the initial rapid reaction is fully investigated. Any calculations performed on this data assuming a calibration plot of concentration of TCMP against absorbance is valid could later be proved incorrect, when the kinetic parameters of the initial rapid reaction are identified. So without kinetic information on this initial rapid reaction (i.e. the first 1 s of the reaction), in depth analysis of the results would be unwise.

6.8 Mechanism Of The Stage Two Reaction

The mechanism of the first stage of the reaction, that is the addition of isoprene (the diene) to phosphorus trichloride (the dienophile) is effectively a modified Diels–Alder reaction, referred to as the McCormack 1,4– cycloaddition reaction. As mentioned earlier (see section 1.8.1 and 2.0), the McCormack cycloaddition can proceed with high product specificity with respect to the position of the double bond and these results have been documented [Quin, L.D. 1968].

However the mechanism of the second stage of the reaction, that is the addition of methanol to the product of the first stage of the reaction, the intermediate halophosphonium halide compound 1,1,1–trichloro–3 methyl–3–phospholene, is far from understood and has not been previously investigated. Speculation as to the generally supposed mechanism for this type of reaction have been made [Hasserodt, U. 1963 and Quin, L.D. 1968] but no precise mechanism has been substantiated.

The Chemometric analysis and kinetic investigations of the second stage of the reaction yielded valuable insight into the nature of the mechanism involved. The information inferred from the experiments was that,

i) An advantageous temperature change from -10°C to 25°C, after addition of alcohol increases the yield of product.

ii) Acidic conditions are preferred to basic conditions.

iii) The neutralisation necessary for the extraction phase does not influence the reaction, only the extraction yield of the product.

iv) A slow addition of methanol to low concentrations of the intermediate at a low temperature reduces the yield of the product.

v) A noticeable immediate colour change in the solution of the intermediate in methylene chloride occurs upon addition of the alcohol (reduction in the colour intensity).

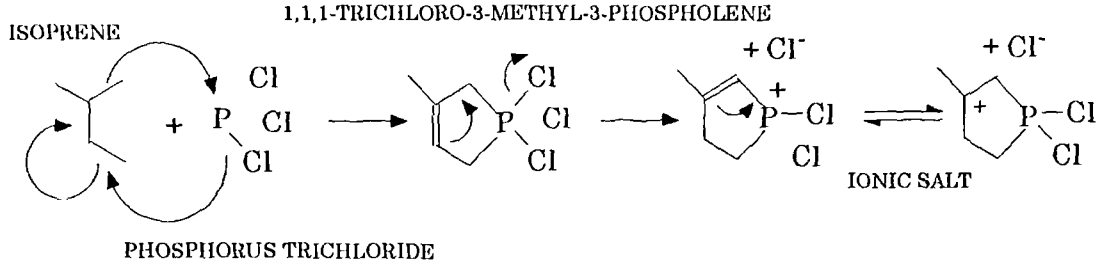
vi) The reaction is very exothermic.

vii) A very fast initial addition reaction occurs, the speed of this initial reaction implies that reaction must be ionic.

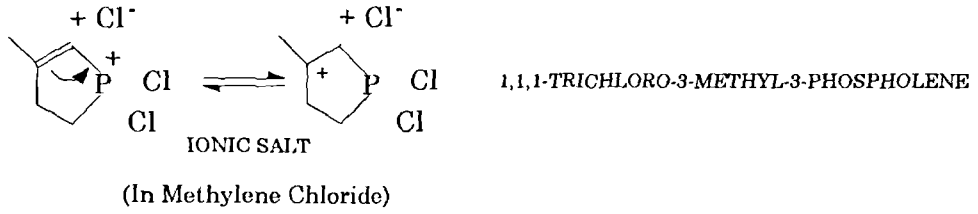
viii) The subsequent formation of the product occurs much more slowly.

These inferences were assimilated and the mechanism shown in Figure 86 is proposed as a possible explanation. The first step of this mechanism is an initial rapid addition of methanol (rate constant k_1) followed by a subsequent slower dealkylation (rate constant k_2), by the by–product of the reaction, hydrogen chloride, to generate methyl chloride. These two reactions are enhanced by the low temperature of -10°C, the succeeding secondary addition of methanol (rate constant k_3) proceeds slowly and is enhanced by a higher temperature of 25°C (room temperature). The extraction phase involving saturated sodium hydrogen carbonate solution does not participate in the reaction, it only aids in the extraction of the product, by increasing the amount retrieved. All the steps in the mechanism can occur at low and high temperatures but the greatest conversion of reactants to product is achieved by an initial low addition temperature for a short time and then a higher stirring temperature for a longer time.

STAGE I



STAGE II



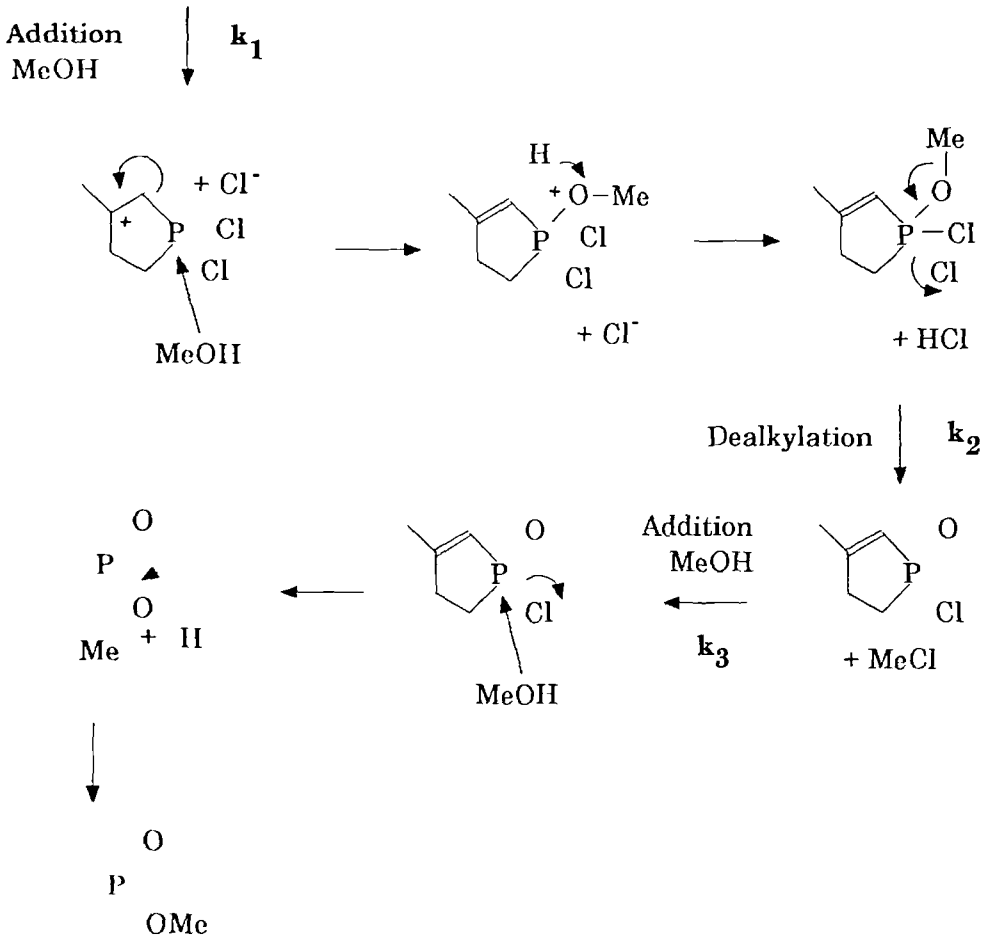


Figure 86 Mechanisms Proposed For Stage I And II Reactions

Further evidence in support of this reaction mechanism was obtained by the mass spectrometric identification of methyl chloride (boiling point -24°C) in the evolved gaseous products of the reaction. The reaction was conducted on a small scale in an evacuated glass vessel connected to the mass spectrometer via a liquid nitrogen cold trap and an aromatic chlorinated solvent bubbler trap (aromatic chlorinated solvents are ideal for trapping alkyl chlorides). Subsequently the traps were warmed and the trapped material passed into the mass spectrometer for analysis. Figure 87 shows the mass spectrum obtained and confirms the presence of methyl chloride as a major product.

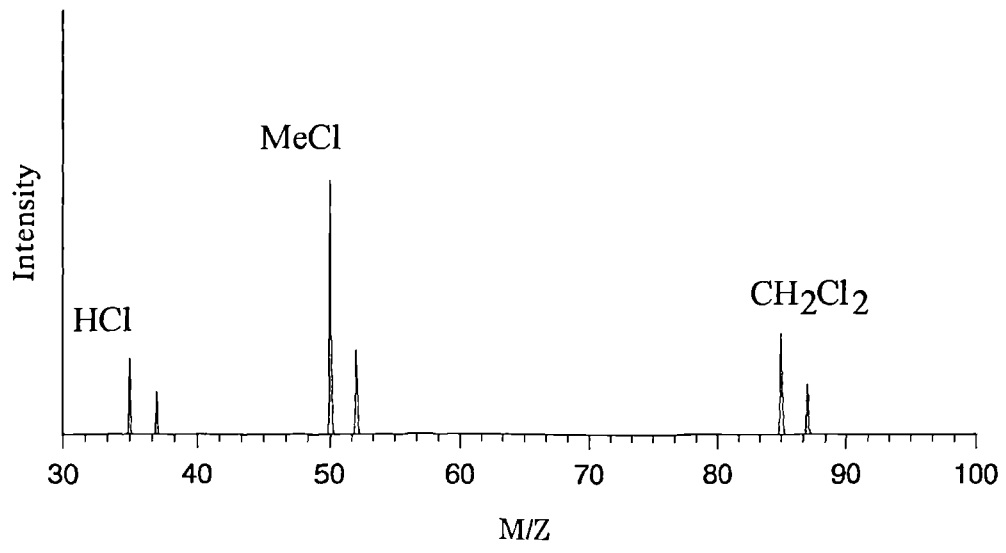


Figure 87 Mass Spectrum (70 eV) Of Gaseous Products Of Stage II Reaction

7.0 Overall Conclusions

The major objectives of the work undertaken were to synthesise heterocyclic phosphorus compounds based on the phospholene oxide ester structure and to assess their ability as flame retardants for polyurethanes.

- The first objective was achieved, with a final overall yield of 80 % (optimised from the initial 10 %) over the two stage synthesis process, for the initial novel target compound. Due to the complex multivariate interaction between the reaction variables it is extremely unlikely that this optimisation could have been achieved without the use of Chemometric techniques. Three further analogues were also synthesised.

- These along with the initial novel target compound, were incorporated into polyurethane foam formulations. They could not be incorporated into flexible foams, as their inclusion affected the foam's structure and caused the foams to "collapse". However, they were successfully incorporated into rigid foam formulations at various addition levels.

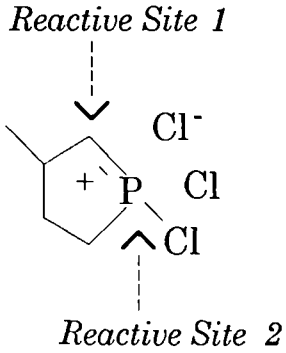
- The novel flame retarded rigid polyurethane foams performed extremely favourably in all of the three flamability tests undertaken when compared to currently available alternatives. Their flame retardant properties were not only influenced by the high percentage phosphorus content as expected, but also by the alkyl ester group. Quite how the alkyl ester group affects their flamability performance is unknown, but this fact should definitely be noted.

- The thermal stability of all the phospholene oxide esters could be the cause of this incompatibility problem with flexible polyurethane foam formulations as mentioned in section 6.0. A phospholene oxide ester with a higher thermal stability than those already synthesised would perhaps out perform, in terms of flame retardant ability, the other phospholene oxide esters already tested.

7.1 Suggestions For Future Work And Additional Studies

The original work accomplished thus far has laid the foundations on which to build a successful new novel non–halogenated flame retardant for polyurethane foams.

From these conclusions it therefore appears necessary to synthesise compounds with greater thermal stability and still maintain a high phosphorus content. Using the intermediate compound 1,1,1–trichloro–3–methyl–3–phospholene as a starting reactant and reacting with other phosphorus containing compounds e.g. $POCl_3$, or other phosphorus flame retardants, it should be possible to synthesise new compounds with a high phosphorus content and high thermal stability. There are two potential reactive sites on this intermediate molecule, only one (i.e. site 2) of which has been partially investigated.



Each of these reactive sites is open to exploitation. Since the limited family of phospholene oxide esters already synthesised have performed well as novel flame retardants for polyurethane foams, then further work directed at specific target molecules will surely result in other successful novel flame retardants being synthesised. These could prove to be more compatible with flexible polyurethane foams. The flammabilty test results also indicated that the alkyl ester group played an important part in the flame retardant behaviour of the novel compounds, as well as their inherently high level of phosphorus content and so any subsequent developments should utilise this fact.

Some areas definitely worth further investigation and development are,

- Reaction of the intermediate 1,1,1–trichloro–3–methyl–3–phospholene with ethylene or propylene oxide to hopefully link two intermediate molecules together.

- Reaction of phosphorus trichloride with dicyclodienes e.g. dicyclopentadiene, could yield complex compounds, which when reacted further would yield compounds with a high molecular weight and hence favourable thermal stability and yet still retain the high degree of phosphorus content required.

- Reaction of the intermediate 1,1,1–trichloro–3–methyl–3–phospholene with different nucleophiles and electrophiles.

7.1.1 Trans–Esterification Reactions

Trans–esterification reactions using longer chain diols e.g. diethylene glycol and triethylene glycol with sodium alkoxide or inorganic ester catalysts, might yield the anticipated products (see section 6.2). However any compounds synthesised will almost certainly have similar thermal stability to the four phospholene oxides already synthesised and so may prove to be incompatible with flexible foams.

7.1.2 Optical Activity Of Phospholene Oxide Esters

It was believed that the phosphorus atom in the new molecules synthesised could be optically active. However polarimetry studies of all the phospholene oxide esters synthesised showed no evidence of optical rotation, unless of course 50/50 racemic mixtures were formed.

7.1.3 Kinetics Of Stage II Reaction

The rapid initial reaction which occurs over approximately the first 200 ms following the mixing of 1,1,1–trichloro–3–methyl –3–phospholene and methanol, has yet to be isolated. New dedicated stop–flow equipment needs to be designed and constructed to overcome the problems detailed earlier in section 6.6. All the kinetic data obtained thus far is valid only for the reaction occurring later than 1 s after mixing of the reactant.

References

Abou–Donia, M.B.and Lapadula, D.M., *Ann. Rev. Pharmacol. Toxicol.*, **30**, 405 (1990)

Albright & Wilson, *PO Box 80, Trinity Street, Oldbury, Birmingham, B69 4LN* 021 541

Arbuzov, B.A., *Zhurnal Obshchei Khimii*, **51**, 1705 (1985)

Arbuzov, B.A., Vizel, A.O., Giniyatullin, R.S., Shchukina, L.I. and Anoshina, N.P., *Zhurnal Obshchei Khimii*, **45**, 512 (1975)

Barker, R.H. and Hendrix J.E., *Flame Retardancy Of Polymeric Materials*, **Vol 5**, Dekker, New York (1979)

Batt, A.M. and Appleyard, P., *J. Fire Sciences*, **7**, 338 (1989)

Bamford C.H. & Tipper C.F.H. *Comprehensive Kinetics*, Elsevier (1965)

Berestovitkaya, U.M., *Zhurnal Obshchei Khimii*, **51**, 2418 (1981)

Bertelli, G. and Locatelli, R, *U.S. Patent Office*, **4,579,894** (1986)

Bond, A., Green, M. and Pearson, S.C., *J. Chem. Soc. B*, 929 (1968)

Box, G.E.P and Draper, N.R, *Evolutionary Operation*, Wiley, New York (1969)

Box, G.E.P., *Statistics For Experimenters*, Wiley & Sons, New York (1978)

Caldin, E.F., *Fast Reactions in Solution*, Blackwell Scientific Publications, Oxford (1964)

Carlson, R., *Chem. Scripta*, **27**, 545 (1987)

Carnahan, J., Haaf, W., Nelson, G., Lee, G., Abolins, V. and Shank, P., *Paper Presented At Proc. 4th Intl. Conf. Flammability And Safety*, **Product Safety Corp.**, San Francisco (1979)

Chase, W.W. *Text.World*, **93**, 90 (1943)

Cittern, P., *Albright And Wilson Ltd*, **Project 41**, December 1987

Conklin, M.N. *Colour Trade J.*, **11**, 171 (1922)

Daniel, C, *Technometrics*,**1**, 311 (1959)

Davies, O.L., *Design And Analysis Of Industrial Experiments*, ICI/Oliver And Boyd, London (1954)

Davies, P.M., *A Systematic Approach To Phosphorus Based Flame Retardants*, **Paper Presented At Industrial Inorganic Chemicals Group**, RSC, 13th January (1993)

De Leon, N. and Marston, C.C., *J. Chem. Phys.*, **91**, 3405 (1989)

Dodd, J.W. and Tonge, K.H., *Thermal Methods*, Wiley & Sons, Chichester (1987)

Duckworth, W.E., *Statistical Techniques In Technological Research*, Methuen, London (1968)

Farman, J.C., Gardiner, B.G., and Shanklin J.D. *Nature*, **315**, 207 (1985)

Fenimore, C.P. and Martin, F.J., *Mod. Plast.*, **44**, 141 (1966)

Flame Retardant Buyers' Guide, *Amer. Dyestuff Reporter*, **January**,13 (1985)

Franklin, M. and Bailey, G., *Appl. Stats.*, **26**, 321 (1977)

Furniture and Furnishing Fire Safety Regulations, *Home Office* (1988)

Greenfield, D., *Appl. Stats.*, **25**, 64 (1976)

Hammond, P.J., Scott, G. and Hall, C.D., *J. Chem. Soc. Perkin Trans. 2*, **2**, 205 (1982)

Harthcock, M.A., Villarreal, J.R., Richardson, L.W. and Laane, J., *J. Phys. Chem.*, 88, 1365 (1984)

Hasserodt, U., Hunger, K. and Korte, F., *Tetrahedron*, **19**, 1563 (1963)

Hastie, J.W., *J. Res. Nat. Bur. Stand.*, **77**, 733 (1973)

Hoefer, F., *Histoire de la Chemie*, Paris, **2**, 183 (1843)

Hunger, K., Hasserodt, U. and Korte, F., *Tetrahedron*, **20**, 1593 (1964)

Hunt, W.H. *The Chemical Engineer*, **11**, 22 (1910)

Kay, M., Price, A.F. and Lavery, I., *J. Fire Retard. Chem.*, **6**, 69 (1979)

Kemp, D.D. *Global Environmental Issues*, Routledge, London (1990)

Kuryla, W.C., Papa, A.J. *Flame Retardancy Of Polymeric Materials*, **Vol 4**, Marcel Dekker, New York (1978)

Kuryla, W.C., Papa, A.J. *Flame Retardancy Of Polymeric Materials*, **Vol 5**, Marcel Dekker, New York (1979)

Lewin, M., *Flame Retardance Of Fabrics*, **Vol 2**, Marcel Dekker, New York (1984)

Mann, F.G., *The Heterocyclic Derivatives Of Phosphorus, Arsenic, Antimony and Bismuth*, Wiley-Interscience, New York (1970)

Marston, C.C and De Leon, N., *J. Chem. Phys.*, **91**, 3392 (1989)

McCormack, W.B., *U.S. Patent Office*, **2,663,736 & 3,663,737** (1953)

Moedritzer, K., *Canadian Patent Office*, **958,145** (1974)

Moedritzer, K.and Miller, R.E., *Syn. React. Inorg. Metal-Org. Chem.*, **5**, 299 (1975)

Moedritzer, K.and Miller, R.E., *Syn. React. Inorg. Metal-Org. Chem.*, **7**, 311 (1977)

Moedritzer, K.and Miller, R.E., *Syn. React. Inorg. Metal-Org. Chem.*, **8**, 167 (1978)

Molina, M.J. & Rowland, F.S. *Nature*, **249**, 810 (1974)

Montgomery, L.C., *Design And Analysis of Experiments*, Wiley (1984)

Muir, D.C.G., *Phosphate Esters, Anthropogenic Compounds, Handbook Of Environmental Chemistry*, **Vol. 3**, Springer–Verlag, Berlin (1984)

Müller, E.W. and Korte, F., *Tetrahedron Letters*, **No. 41**, 3039 (1964)

Myers, D.K. and Quin, L.D., *J. Org. Chem.*, **36**, 1285 (1971)

Nelb, R.G., *U.S. Patent Office*, **4,738,990** (1988)

Onder, S., *U.S. Patent Office*, **4,156,065** (1979)

Perkin, W.H. *J. Ind.Eng.Chem.*, **5**, 57 (1913); Text. Mfr., **39**, 423 (1913)

Peters, H., *Arch. Geschichte Naturw.*, **4**, 206 (1912)

Price, D., Horrocks, A.R. and Tunc, M., *Chem. Brit.*, **March**, 235 (1987)

Quin, L.D., Gratz, J.P. and Barket, T.P., *J. Org. Chem.*, **33**, 1034 (1968)

Ramsbottom, J.E. & Department Of Scientific And Industrial Research, *The Fireproofing of Fabrics*, London, H.M.S.O. (1947)

Saeger, V.W., Hicks, O., Kaley, R.G., Michael, P.R., Mieure, J.R. and Tucker, E.S., *Envir. Sci. Tech.*, **13**, 840 (1979)

Schmude, R.W., Harthcock, M.A., Kelly, M.B. and Laane, J., *J. Molecular Spectroscopy*, **124**, 369 (1987)

Schwindt, M.A., Lejon, T. and Hegedus, L.S., *Organometallics*, **9**, 2814 (1990)

Smith, C.P., U.S. *Patents Office*, **3,767,708** (1973)

Soderlund, E.J., Dybing, E., Holme, J.A., Hongslo, J.K., Rivedal, E., Sanner, T. and Nelson, S.D., *Acta. Pharmacol. Et Toxicol.*, **56**, 20 (1982)

Tesoro, G.C., *J. Appl. Polym. Sci.*, **13**, 283 (1978)

UK Fire Statistics, *Home Office* (1991)

Vizel, A.O., Krupnov, V.K., Arbuzov, B.A. and Fadeeva, L.M., *Zhurnal Obshchei Khimii*, **43**, 2137 (1973)

Ward, F., *J.Soc.Dyers Colour.*, **71**, 569 (1955)

Watson–Marlow Limited, *Falmouth, Cornwall TR11 4RU England*, ☎0326 73461

Weil, E.D., *Flame Retardancy Of Polymeric Materials*, **Vol 3**, Dekker, New York (1975)

Weil, E.D., *Flame Retardants (Phosphorus) In Kirk-Othmer Encyclopedia Of Chemical Technology Volume 10*, Wiley & Sons, New York (1980)

Weil, E.D., *Flame Retardants Based On Phosphorus*, **Paper Presented At BCC Conference On Flame Retardancy**, Stamford, 14th May (1991)

Weitkamp, H. and Korte, F., *Z. Anal. Chem.*, **204**, 245 (1964)

Wohler, F., *Ann. Physik*, **12**, 253 (1828)

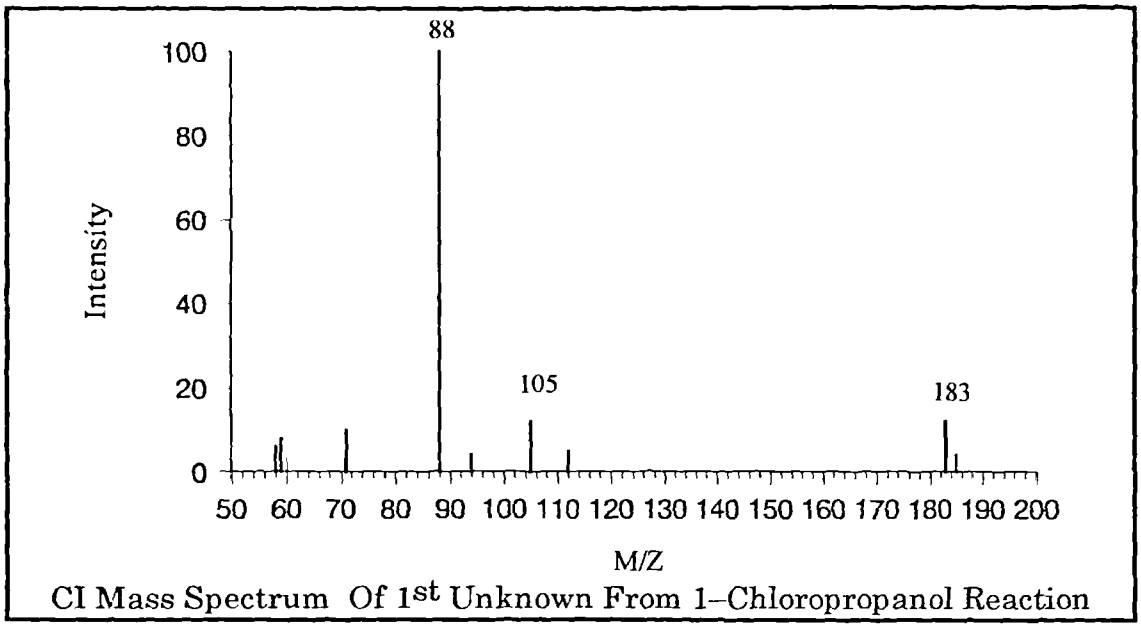
Woods, G., *The ICI Polyurethanes Book*, John Wiley & Sons, Chichester (1990)

Woolley, D., *Chemistry In Britain*, **March**, 215 (1987)

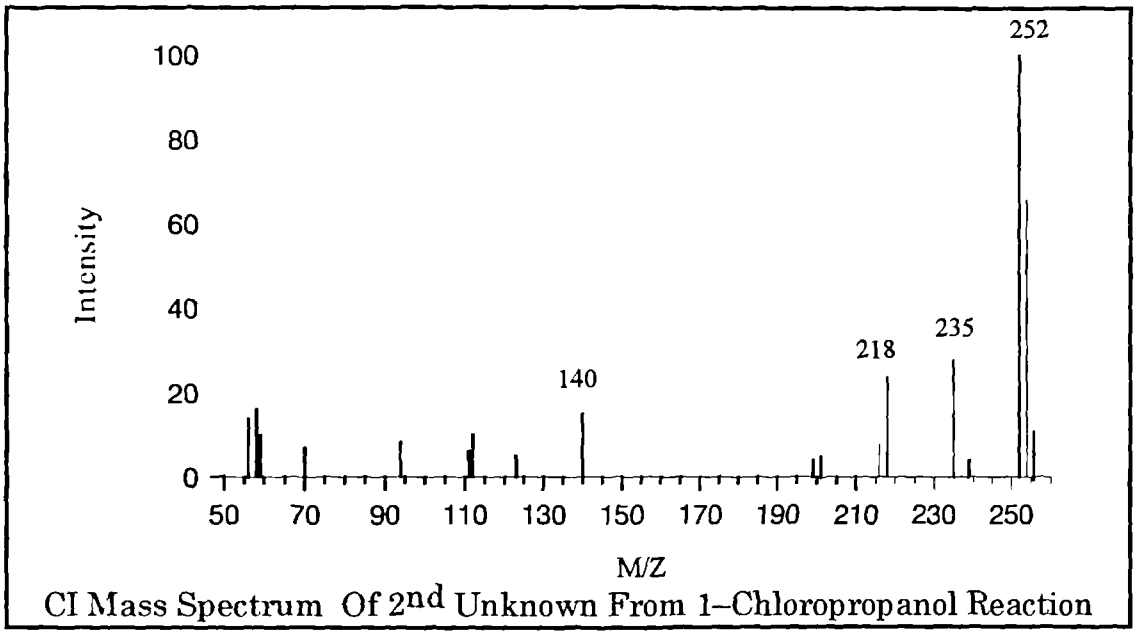
Zeleznick, L.D., Myers, T.C. and Titchener, E.B., *Biochem. Biophys. Acta*, **78**, 546 (1963)

Appendix : Assorted Spectra Of Compounds Synthesised

Instruments used : Perkin Elmer 1710 FTIR, Bruker A.C. 300 MHz NMR, Finnigan 4500 MS (CI reagent gas ammonia) and Varian 3400 GC.



CI Mass Spectrum Of 1st Unknown From 1–Chloropropanol Reaction



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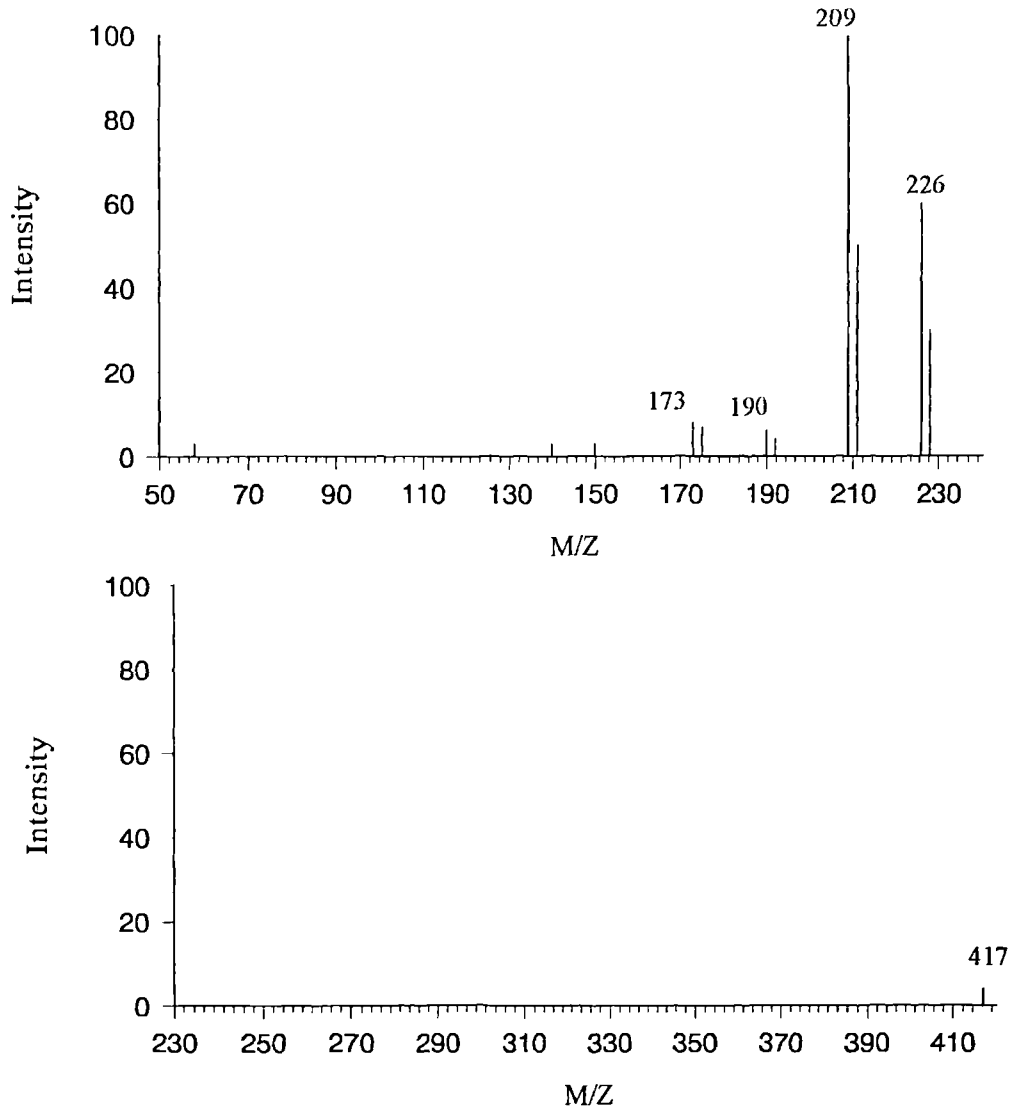
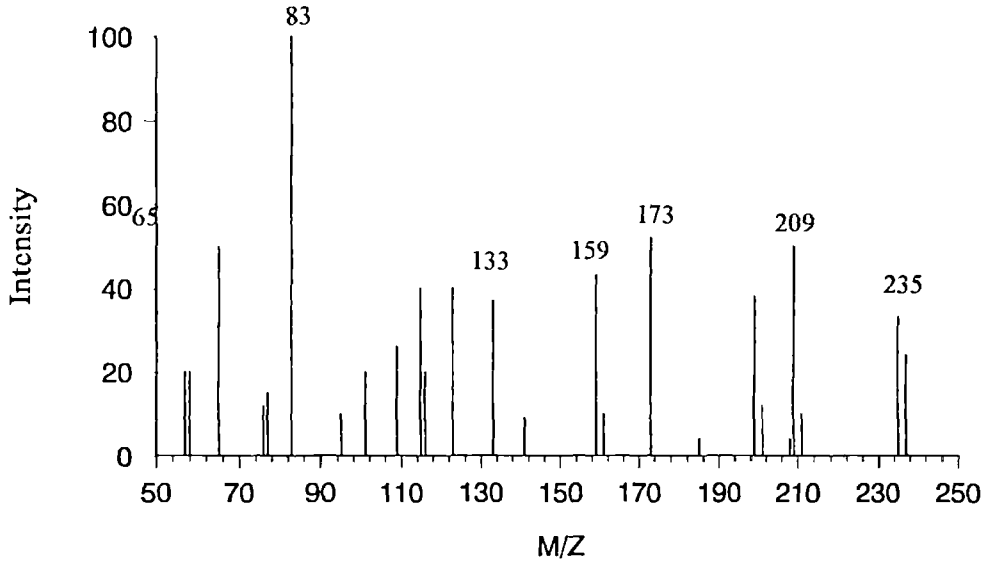
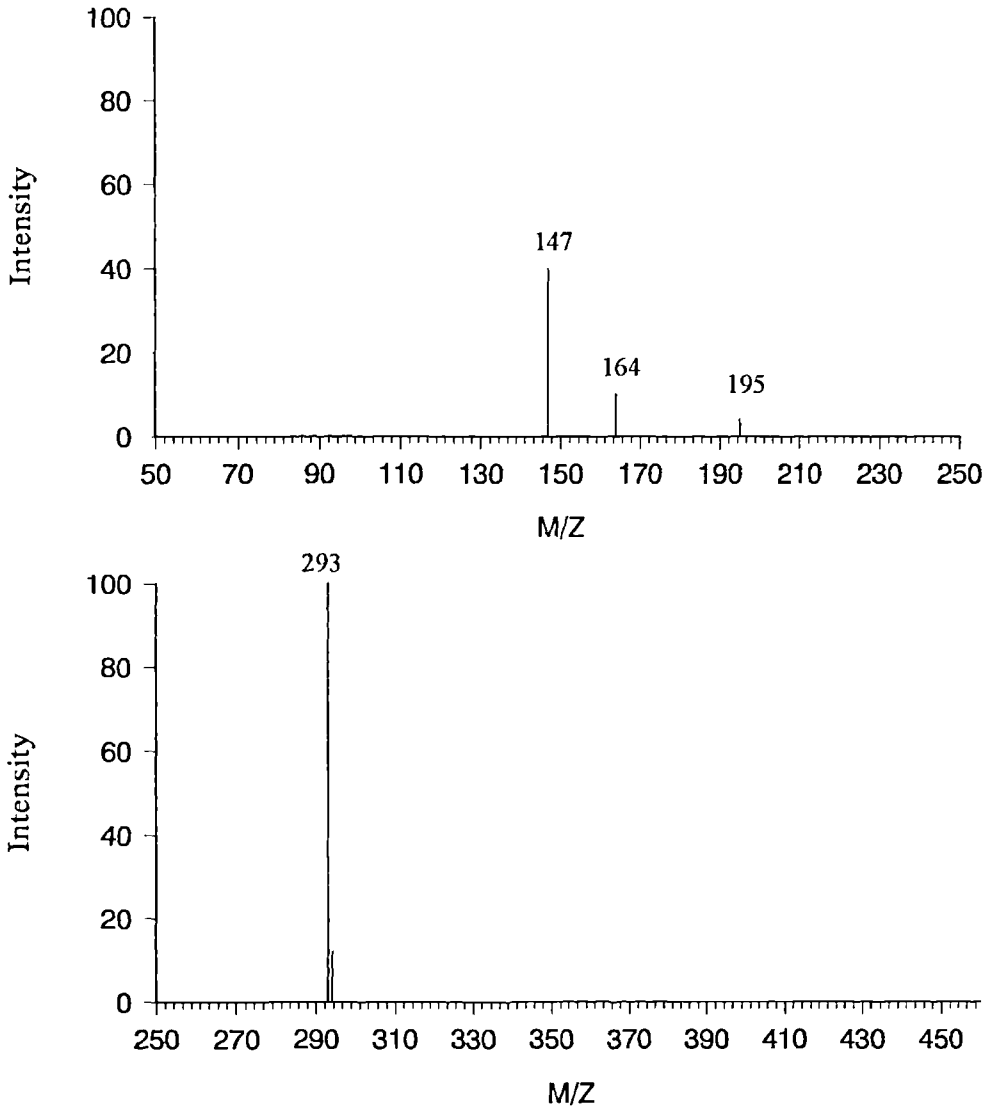


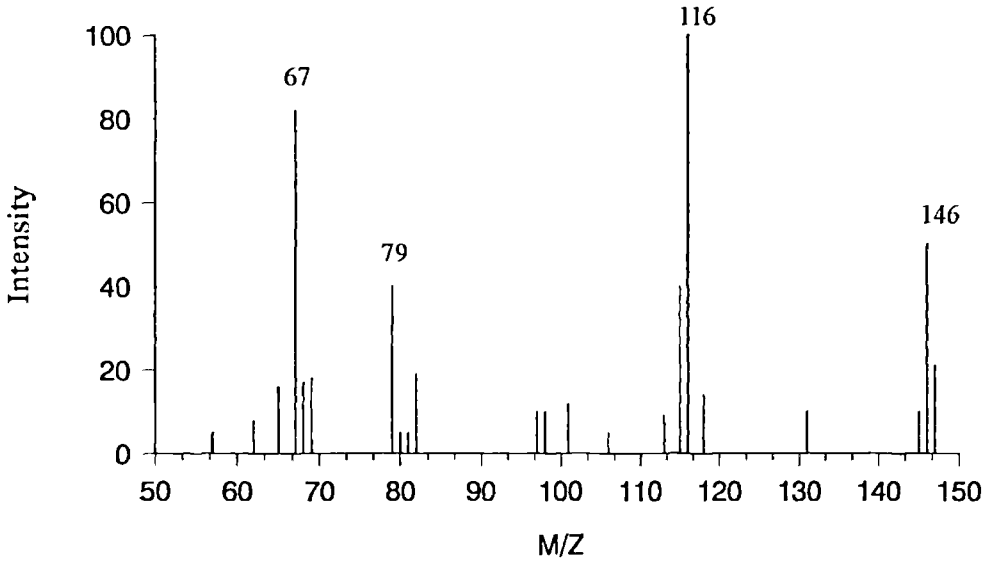
CI Mass Spectrum Of 1–Chloropropoxy–3–Methyl–2–Phospholene Oxide (3rd Unknown) From 1–Chloropropanol Reaction



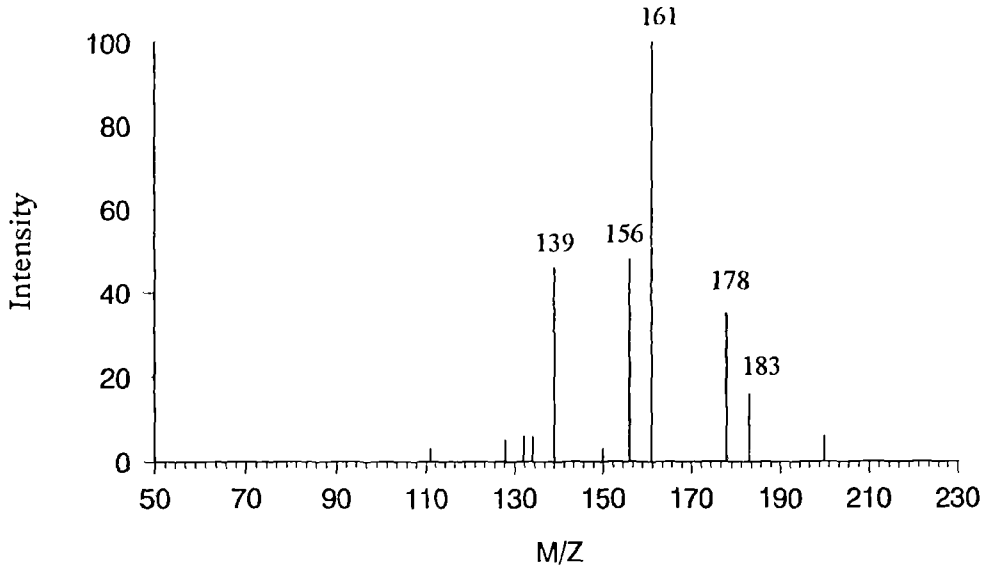
EI Mass Spectrum (70 eV) Of Products Of 1–Chloropropanol Reaction

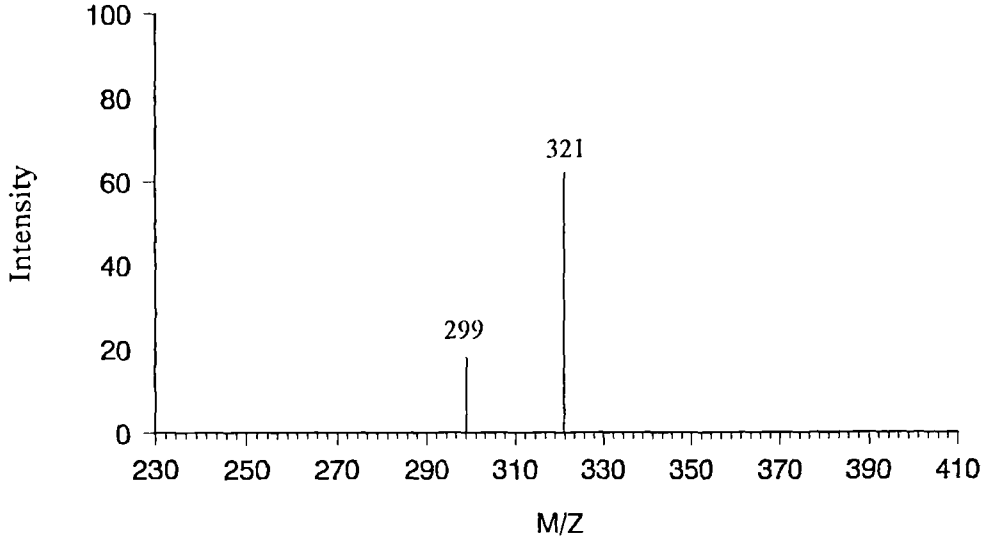


CI Mass Spectrum Of 1–Methoxy–3–Methyl–2–Phospholene Oxide

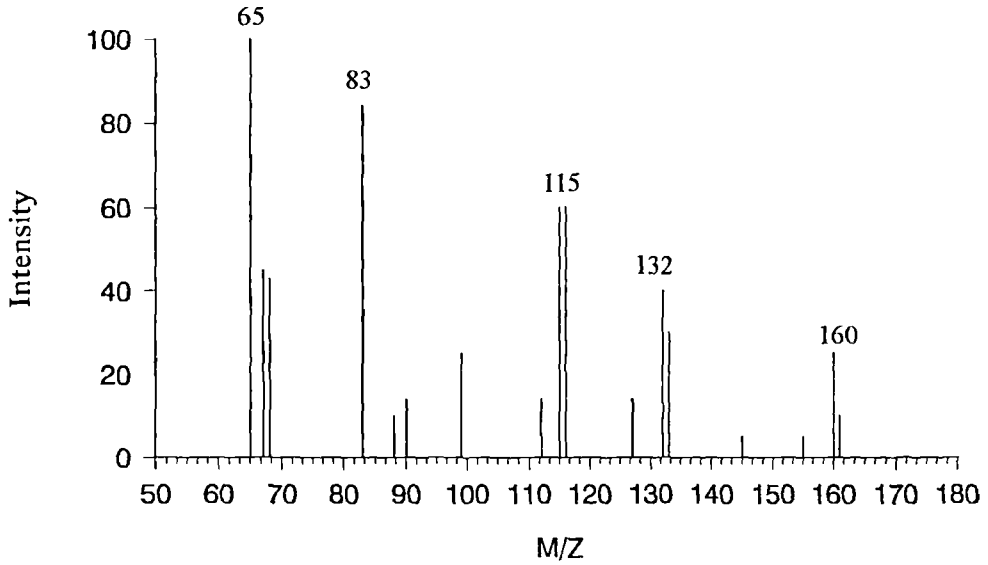


EI Mass Spectrum (70 eV) Of 1–Methoxy–3–Methyl–2–Phospholene Oxide

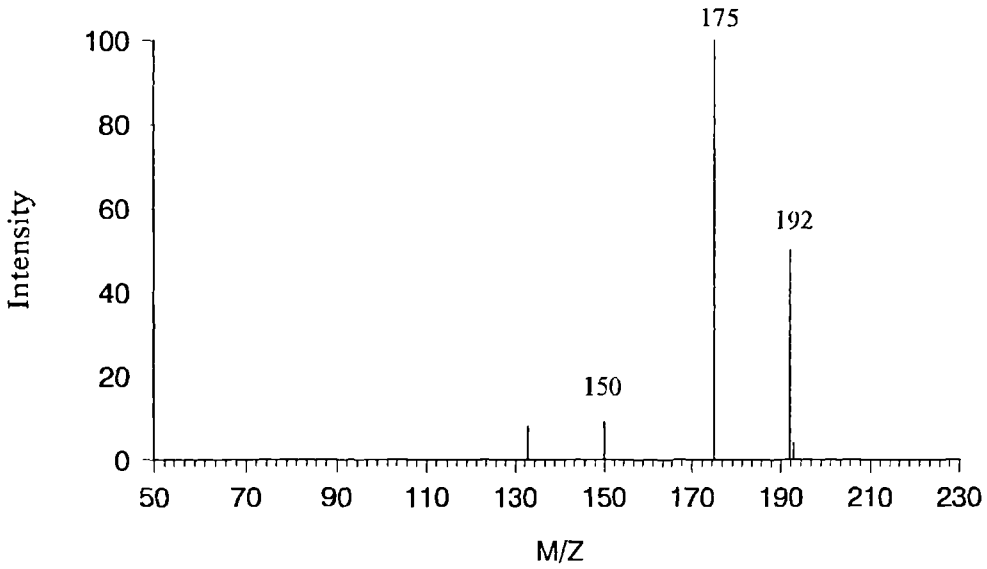


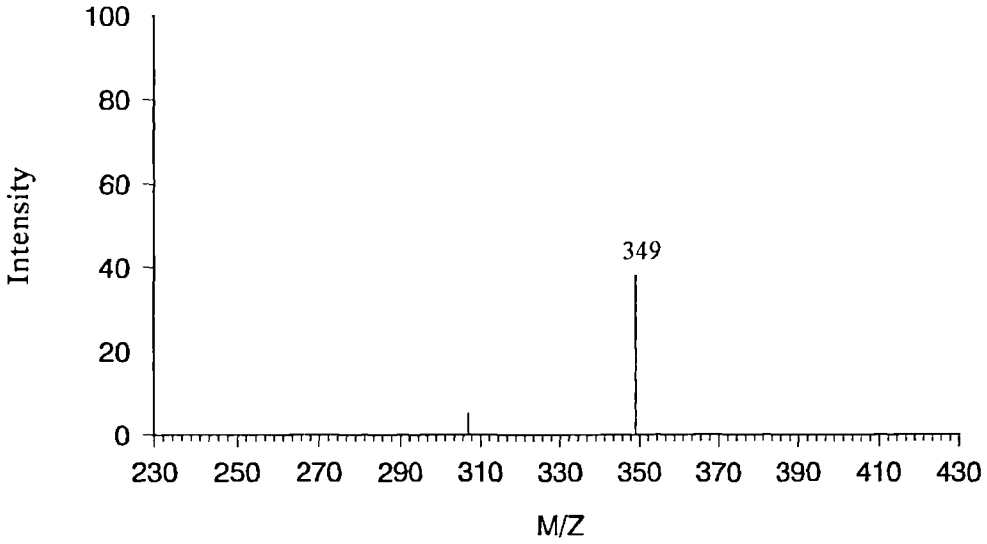


CI Mass Spectrum Of 1–Ethoxy–3–Methyl–2–Phospholene Oxide

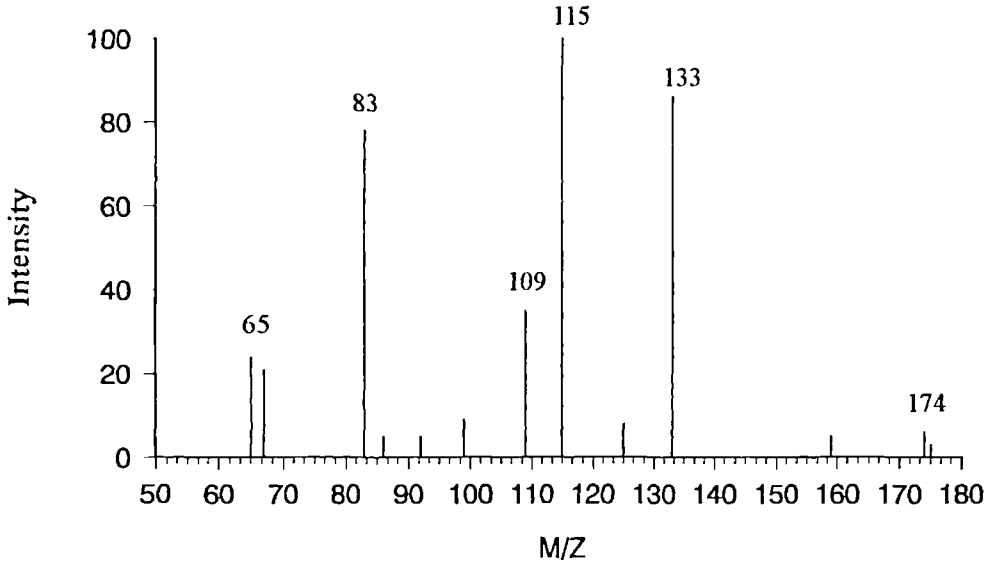


EI Mass Spectrum (70 eV) Of 1–Ethoxy–3–Methyl–2–Phospholene Oxide

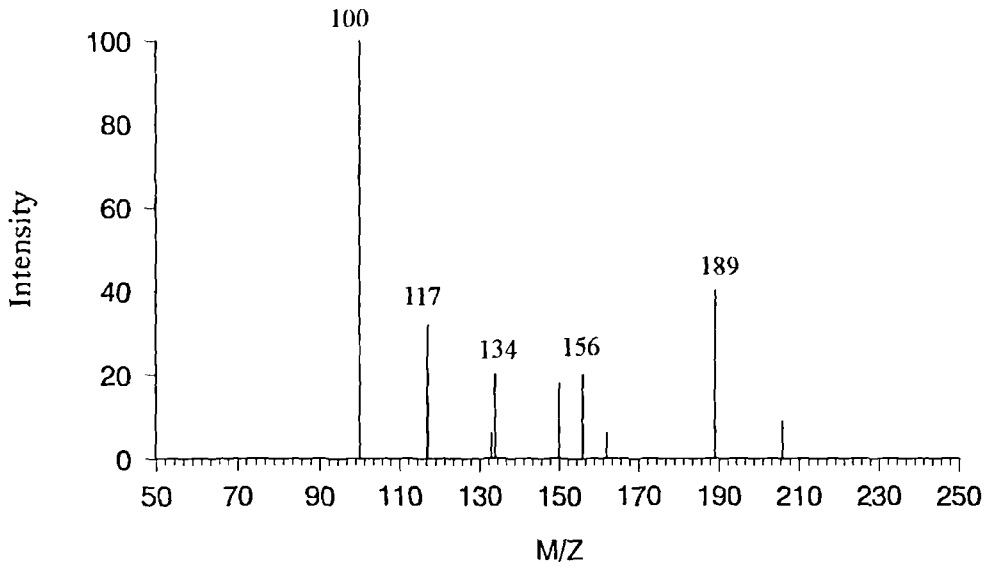


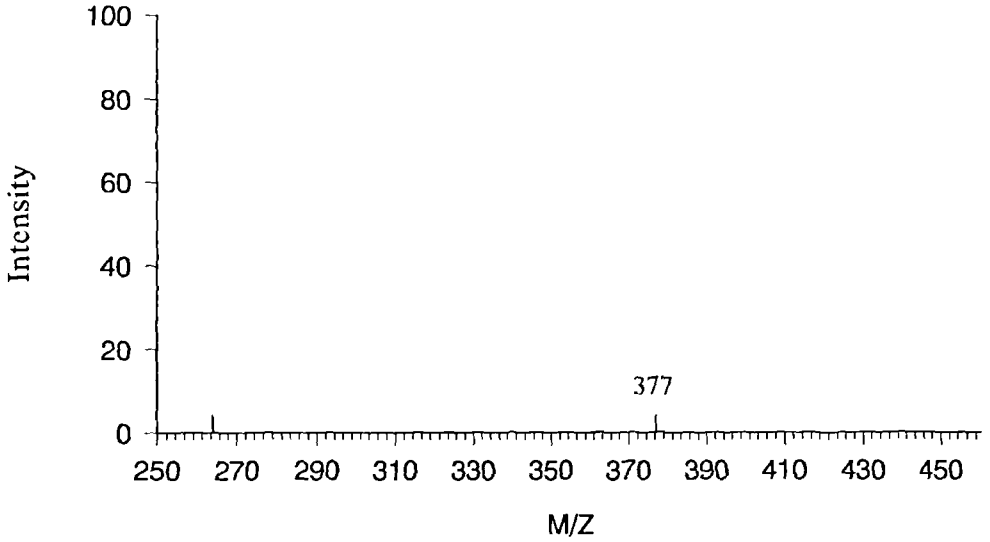


CI Mass Spectrum Of 1–Ispropoxy–3–Methyl–2–Phospholene Oxide

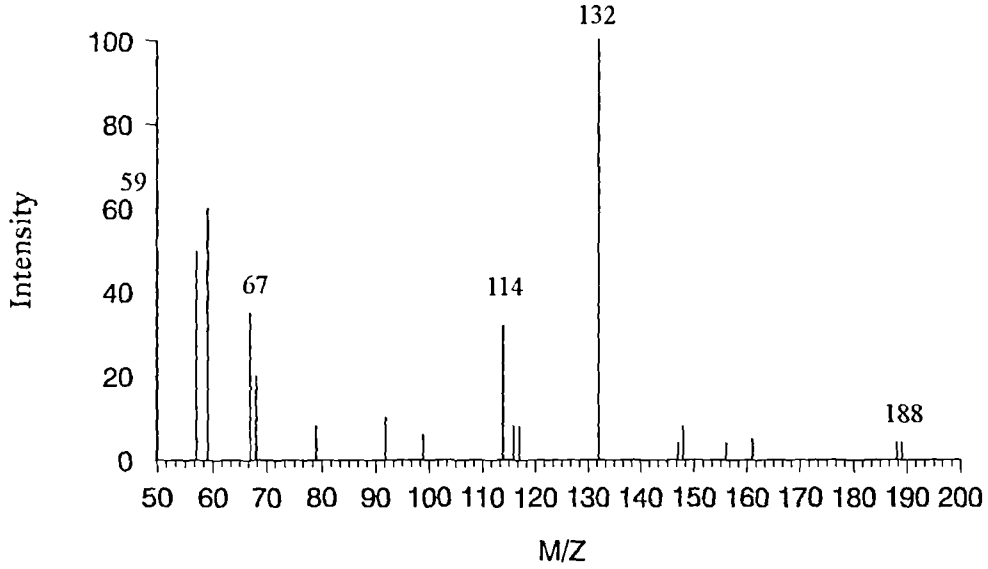


EI Mass Spectrum (70 eV) Of 1–Ispropoxy–3–Methyl–2–Phospholene Oxide

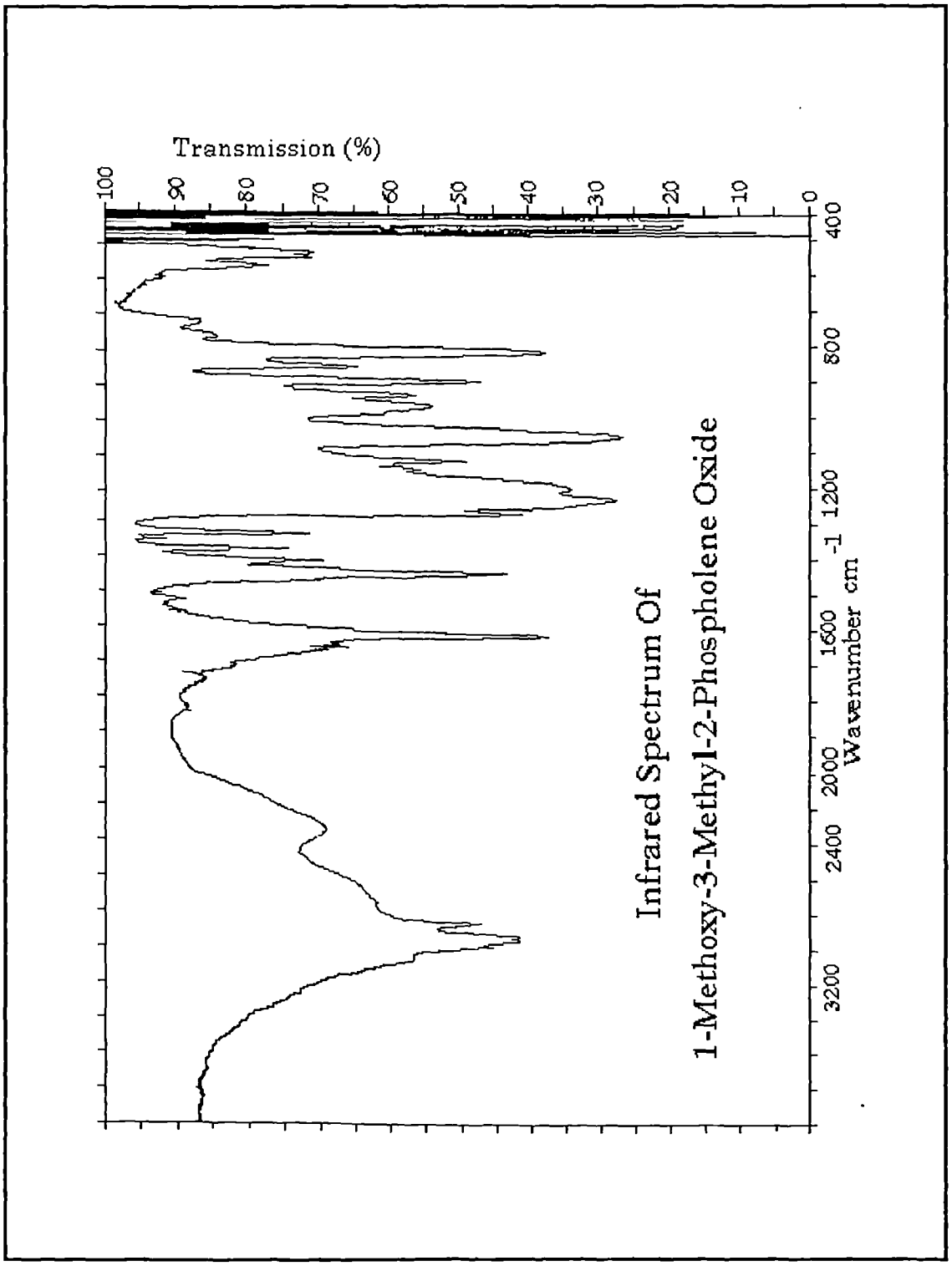


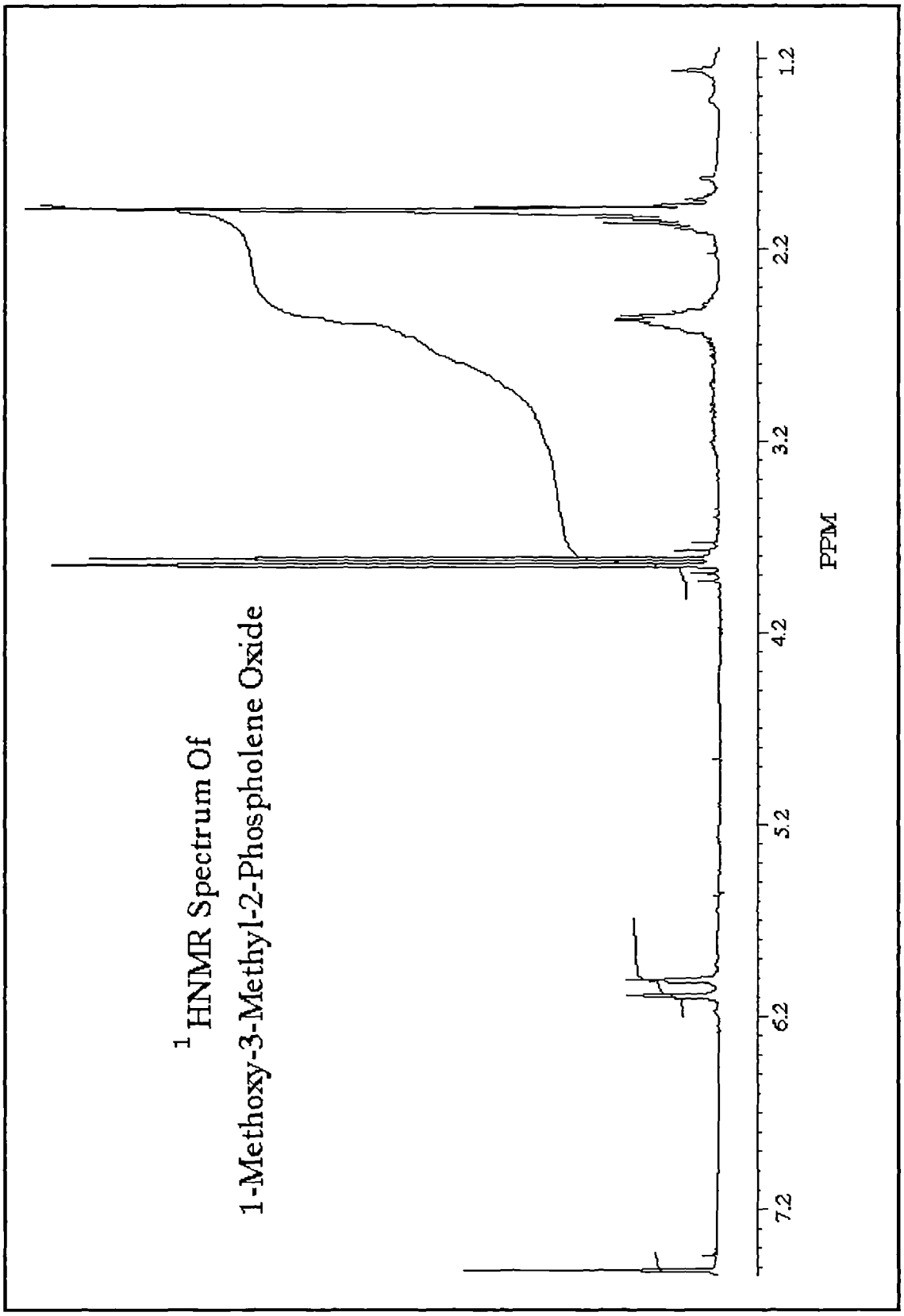


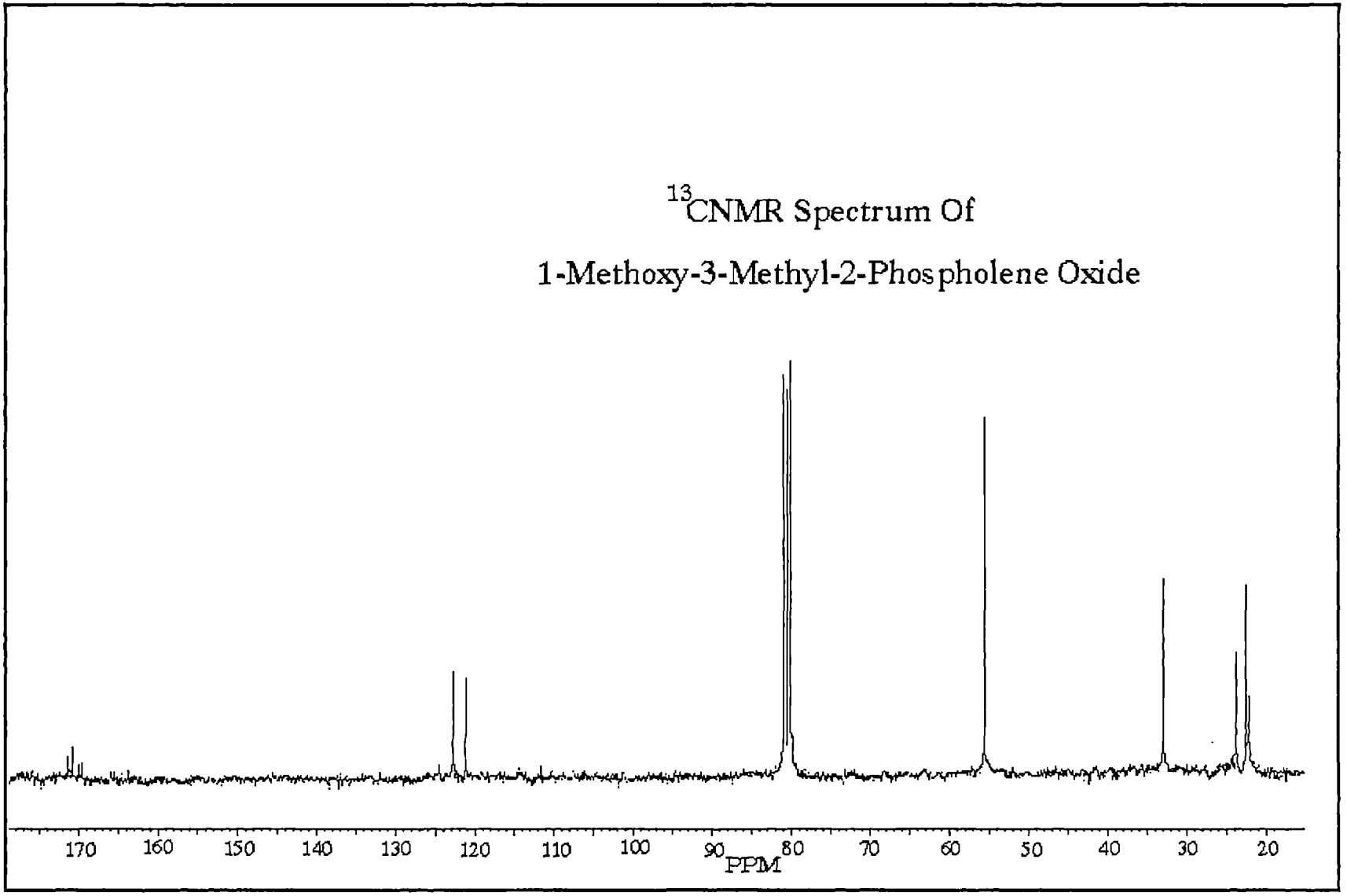
CI Mass Spectrum Of 1–Tertbutoxy–3–Methyl–2–Phospholene Oxide



EI Mass Spectrum (70 eV) Of 1–Tertbutoxy–3–Methyl–2–Phospholene Oxide

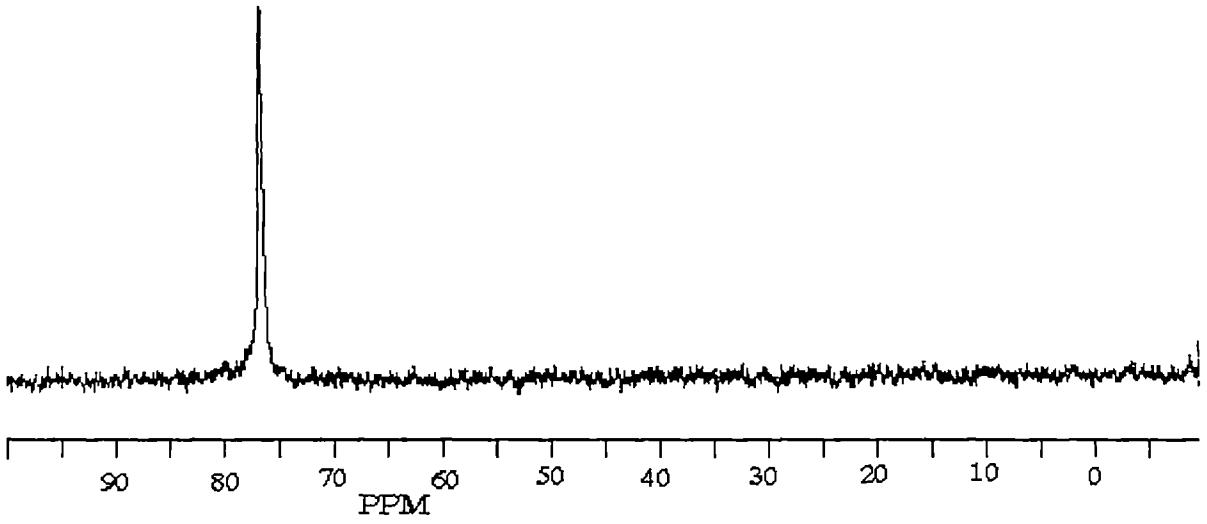

Transmission (%)
100
90
80
70
60
50
40
30
20
10
0
400
800
1200
1600
2000
2400
3200
Wavenumber cm -1
Infrared Spectrum Of
1-Methoxy-3-Methyl-2-Phospholene Oxide


1 HNMR Spectrum Of
1-Methoxy-3-Methyl-2-Phospholene Oxide
7.2
6.2
5.2
4.2
3.2
2.2
1.2
PPM


^{13}CNMR Spectrum Of
1-Methoxy-3-Methyl-2-Phospholene Oxide
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
PPM

^{31}PNMR Spectrum Of

1-Methoxy-3-Methyl-2-Phospholene Oxide



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Statement of inventorship and of right to grant of a Patent

Form 7/77

Patents Act 1977

❶ Application details

1a Please give the patent application number *(if known)*: 9201765.6

1b Please give the full name(s) of the applicant(s):
ALBRIGHT & WILSON LIMITED

❷ Title of invention

2 Please give the title of the invention: PHOSPHOLENE OXIDES

❸ Derivation of right

3 Please state how the applicant(s) derive(s) the right to be granted a patent:

By virtue of the inventor's employment

❹ Declaration

4 I believe the person(s) named overleaf (and on any supplementary copies of this form) to be the inventor(s) of the invention for which the patent application has been made. I consent to the disclosure of the details contained in this form to each inventor named.

Please sign here ➡

Signed Colin Kinton Date 20 JAN 93
(day month year)
Colin D. Kinton
Agent for the Applicants

239

031

Please put the full name(s) and address(es) of the inventors in the boxes below:

Please underline the surnames or family names.

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Datum/Date

Zeichen/Ref./Réf.	Anmeldung Nr./Application No./Demande n°.//Patent Nr No./Brevet n°.
	93100865.0-

Anmelder/Applicant/Demandeur//Patentinhaber/Proprietaire
Albright & Wilson Limited

DESIGNATION AS INVENTOR - COMMUNICATION UNDER RULE 17(3) EPC

You have been designated as inventor in the above-mentioned European patent application. Below you will find the data contained in the Designation of Inventor and further data mentioned in Art. 128(5) EPC:

DATE OF FILING : 21.01.93

PRIORITY : GB/28.01.92/ GB 9201765

TITLE : Phospholene oxides

DESIGNATED STATES : AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL PT SE

INVENTOR :
Coleman, Gregory Valentine/17 Church Road, Barton/Torquay, Devon TQ2 8PN/GB
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Horrocks, Arthur Richard/195 Church Road/Bolton, Lancs. BL1 6HJ/GB
Stephenson, James Edward/48 Croftdown Road/Harborne, Birmingham, B17 8RD/GB

DECLARATION UNDER ART. 81 EPC:
The applicant(s) has (have) acquired the right to the European patent as employer(s).

EUROPÄISCHES PATENTAMT DEN HAAG · EUROPEAN PATENT OFFICE THE HAGUE · OFFICE EUROPÉEN DES BREVETS LA HAYE

RECEIVING SECTION

PATENTS ACT 1977

UK Patent Application 92017565.6 on 26th January 1992

PRELIMINARY SPECIFICATION
(Description and Claims)

PHOSPHOLENE OXIDES

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B17 8RD

Applicant's Ref : PF717/GB

PHOSPHOLENE OXIDES

The present invention relates to the synthesis of phospholene oxides.

Such compounds are part of the general class of cyclic phosphorus compounds which, because of their high phosphorus content, are desirable constituents of, e.g. flame retardant compositions.

They have been synthesised but in poor yields with only a few derivatives being prepared. Most literature refers to a reaction scheme involving an alkyl phosphonous dihalide and a diene. In addition poor yields and lengthy reaction times are reported when using phosphorus trichloride and butadiene.

We have now discovered that the above phospholene oxides can be synthesised in substantially improved yields and shortened reaction times.

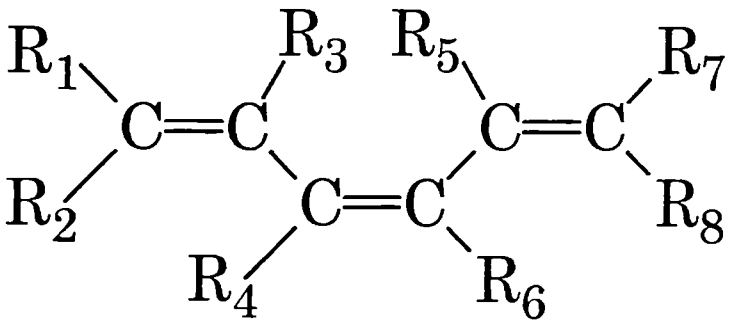
The Invention

In a first embodiment, the present invention provides a method for the production of a phospholene oxide, said method comprising the following stages :

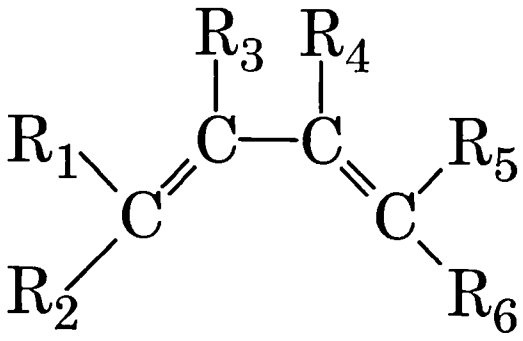
(a) reacting a fully conjugated polyene with a phosphorus trihalide in a dry, inert, oxygen-free atmosphere and at a temperature of from 25°C to 60°C, to form a reaction intermediate ;

(b) labilising said intermediate by means of a solvent and subjecting said labilised intermediate to a further reaction with a nucleophile, in an inert atmosphere and at a temperature of from -70°C to 30°C, to form a phospholene oxide.

In stage (a) the fully conjugated polyene may suitably be a triene of general formula



in which R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 independently represent hydrogen or C_1 to C_{18} alkyl, aryl, alkaryl or aralkyl groups, or, preferably a diene of general formula



in which R_1, R_2, R_3, R_4, R_5 and R_6 independently represent hydrogen or C_1 to C_{18} alkyl, aryl, alkaryl or aralkyl groups, such as butadiene, or especially 2–methyl–1,3–butadiene.

The phosphorus trihalide may suitably be of general formula $PX_1X_2X_3$ in which X_1, X_2 and X_3 independently represent chloride, bromide or iodide, or, more preferably of general formula PX_3 in which X represents iodide, bromide or especially chloride.

Typically in stage (a) of the method according to present invention said conjugated polyene, especially 2–methyl–1,3–butadiene and said phosphorus trihalide, especially phosphorus trichloride, are contacted in a reaction vessel, preferably by dropwise addition of the phosphorus trihalide to the conjugated polyene, in a ratio of from 5:1 to 1.1:1, preferably about 2:1. The dry, inert oxygen-free atmosphere may suitably comprise a gas such as carbon dioxide, argon or nitrogen or a mixture of any of the above, but preferably consists essentially of nitrogen.

In a highly preferred method according to the present invention, said gas, e.g. nitrogen, is introduced into the reaction vessel at an initial vigorous flow rate such that the reactants are agitated, a suitable rate being e.g. 30 ml min^{-1}, which flow rate is decreased such that the loss of volatiles is minimised, a suitable rate being e.g. 4 ml min^{-1}, as the reaction temperature is increased, e.g. by external heating.

Said temperature may typically be of from 0°C to 80°C, such as 25°C to 65°C especially of from 45°C to 55°C. Higher temperatures may be tolerated if a polymerisation inhibitor is included in the reaction mixture such as is conventionally known in the art, e.g. an oil soluble or dispersible copper salt such as a copper salt of a fatty acid, e.g. copper stearate, copper oleate, copper 2–ethylhexoate or copper napthanate or preferably a N-substituted aryl compound, especially 1,2–dinitrobenzene.

It is preferable to exclude any organic solvents from the reaction mixture.

A typical reaction time for the above stage (a) according to the method of the present invention is from 10 to 30 hrs, such as from 15 to 24 hrs, e.g. 20 hrs. The reaction intermediate may be isolated and purified by conventional methods.

In stage (b) of the method according to the present invention, said reaction intermediate may be suitably labilised in an inert atmosphere by means of a solvent such as a chloro-substituted alkyl, aryl, alkaryl or aralkyl compound, especially dichloromethane.

Said nucleophile may typically be an oxygen nucleophile, e.g. a straight or branched chain monohydric alcohol having up to 12 carbon atoms, e.g.

propylene glycol, or ethylene oxide, propylene oxide, phenol, or a substituted phenol, e.g. benzoic acid, nitrophenol or phenylamine. Said nucleophile may alternatively be a nitrogen nucleophile such as a mono-amine or diamine or a sulphur nucleophile such as a thiol or a di-thiol. Oxygen nucleophiles are, however, preferred for the purposes of the present invention.

In a typical method according to the present invention, said nucleophile is contacted in a reaction vessel with said labilised reaction intermediate in a ratio of from 50:1 to 24:1, such as about 25:1, the addition time being from 0 to 40 minutes, such as about 10 minutes, or, more preferably, about 20 minutes.

The inert atmosphere may suitably comprise a gas such as is herein above described with respect to stage (a), typically maintained under a condition of flow, such as at a flow rate of 20 ml min^{-1}.

The temperature of the reaction vessel may range from -70°C to +30°C. However, in a highly preferred method according to the present invention, said nucleophile is added to said reaction intermediate at a temperature of from -15°C to -5°C, preferably of about -10°C, and further reaction is carried out by agitation, e.g. stirring, at ambient temperature.

The reaction may be carried out under basic conditions, e.g. by incorporation of a base such as triethylamine, or under acidic conditions, e.g. by omission of base. It is most preferred to carry out the reaction under acidic conditions, e.g. at a pH of 1.0.

The reaction time may suitably be from 0.5 to 5 hrs, such as 1 hour.

The product phospholene oxide may be isolated and purified according to conventional methods. Typically the reaction mixture is neutralised, e.g., in the case of an acidic reaction mixture, with saturated sodium hydrogen carbonate solution, and the product is recovered by solvent extraction, e.g. with dichloromethane.

Accordingly, the present invention further provides a phospholene oxide produced by the method herein above described.

There is still further provided, accordingly to the present invention, the use of a phospholene oxide produced by the method herein above described as a flame retardant for a polymeric material.

Suitable polymeric materials for the above purposes include polyurethane materials, especially cellular polyurethanes such as flexible or rigid polyurethane foams.

The present invention provides a convenient, high yield route from widely available and relatively inexpensive raw materials to cyclic phosphorus compounds which have considerable commercial potential by virtue of their or their derivatives' foreseeable applicability as e.g. components of flame retardant compositions, detergent formulations or as dispersing agents or wetting agents.

The invention will be further illustrated by the following
Examples :

Example 1

Three moles (261 ml) of phosphorus trichloride were slowly added dropwise to three moles (300 ml) of 2–methyl–1,3–butadiene and 1g of copper stearate polymerisation inhibitor under an initially vigorously flowing dry nitrogen atmosphere. The resulting mixture was then heated to 50°C for 20 hours under a gently flowing atmosphere of dry nitrogen. The deep red/brown solid product was broken up and washed with petroleum ether 40-60 fraction (3x500 ml), yield 500g. IR analysis identified this product as 1,1,1–trichloro–3–methyl–3–phospholene.

To 400 ml of methylene chloride was added 25g (0.125 moles) of 1,1,1–trichloro–3–methyl–3–phospholene and the mixture stirred at -10°C under a flowing atmosphere of nitrogen. Distilled methanol 136 ml (3 moles) was then slowly added over half an hour, the temperature being kept at -10°C and then stirred for 2 hours at -10°C. The solution was then neutralised with saturated sodium hydrogen carbonate solution. The methylene chloride layer was separated and the aqueous layer extracted with methylene chloride (5x200 ml). The organic layers were then recombined and the solvent removed, leaving a dark yellow oil in 83.5% yield, boiling point 75-79°C (0.4 mm). Analysis by GC/MS, ^{1}HNMR, ^{13}CNMR, ^{31}PNMR and IR confirmed it to be 1–methoxy–3–methyl–2–phospholene oxide.

Example 2

1,1,1–trichloro–3–methyl–3–phospholene was prepared earlier as described in Example 1.

To 400 ml of methylene chloride was added 25g (0.125 moles) of 1,1,1–trichloro–3–methyl–3–phospholene and the mixture stirred at -10°C under a flowing atmosphere of nitrogen. Distilled methanol 272 ml (6 moles) was then added over 15 minutes, the temperature being kept at -10°C, then stirred at 25°C for half an hour. The solution was then neutralised with saturated sodium hydrogen carbonate solution. The methylene chloride layer was separated and the aqueous layer extracted with methylene chloride (5x200 ml). The organic layers were then recombined and the solvent removed, leaving a dark yellow oil in 75% yield, boiling point 75-79°C (0.4 mm). Analysis as before showed it to be 1–methoxy–3–methyl–2–phospholene oxide.

CLAIMS

1. A method for the production of a phospholene oxide, said method comprising the following stages :

(a) reacting a fully conjugated polyene with a phosphorus trihalide in a dry, inert, oxygen-free atmosphere and at a temperature of from 25°C to 60°C, to form a reaction intermediate ;

(b) labilising said intermediate by means of a solvent and subjecting said labilised intermediate to further reaction with a nucleophile, in an inert atmosphere and at a temperature of from -70°C to 30°C, to form a phospholene oxide.

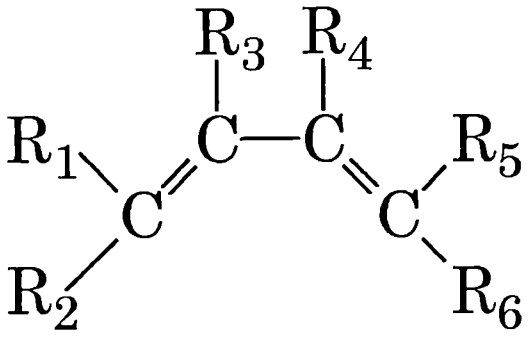
2. A method according to Claim 1, in which the ratio of fully conjugated polyene to phosphorus trihalide in stage (a) is from 5:1 to 1.1:1.

3. A method according to Claim 2, in which said ratio is about 2:1.

4. A method according to Claim 1, 2 or 3, in which the ratio of nucleophile to reaction intermediate in stage (b0 is from 50:1 to 24:1.

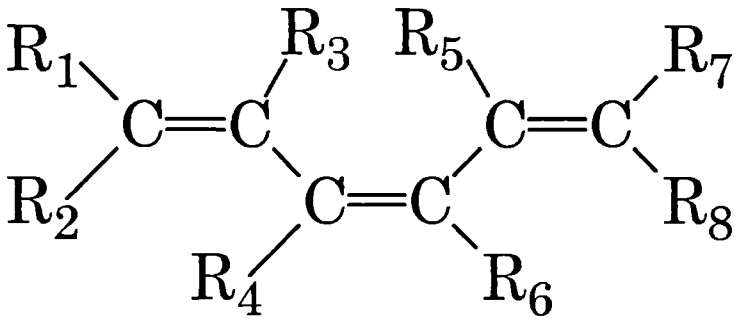
5. A method according to Claim 4, in which said ratio is about 25:1.

6. A method according to any one of the preceding claims, in which the fully conjugated polyene is a diene of general formula.



in which R_1, R_2, R_3, R_4, R_5 and R_6 independently represent hydrogen or C_1 to C_{18} alkyl, aryl, alkaryl or aralkyl groups.

7. A method according to any one of Claims 1 to 5, in which the fully conjugated polyene is a triene of general formula



in which R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 independently represent hydrogen or C_1 to C_{18} alkyl, aryl, alkaryl or aralkyl groups.

8. A method according to any one of Claims 1 to 7, in which the phosphorus trihalide is of general formula $PX_1X_2X_3$ in which X_1, X_2 and X_3 independently represent iodide, bromide or chloride.

9. A method according to any one of the preceding claims, in which the phosphorus trihalide is of general formula PX_3 in which X represents iodide, bromide or especially chloride.

10. A method according to Claim 8 or 9, in which the phosphorus trihalide is phosphorus trichloride.

11. A method according to any one of the preceding claims, in which the conjugated diene is 2–methyl–1,3–butadiene.

12. A method according to any one of the preceding claims, in which the inert atmosphere in stage (a) consists essentially of nitrogen.

13. A method according to any one of the preceding claims, in which the inert atmosphere is initially supplied to the reaction at a flow rate of 30 ml min^{-1}, which flow rate is decreased to 4 ml min^{-1} as the reaction temperature is increased.

14. A method according to any one of the preceding claims, in which stage (a) is carried out at a temperature of from 45°C to 55°C.

15. A method according to Claim 14, in which the temperature is about 50°C.

16. A method according to any one of the preceding claims, in which stage (a) is carried out in the absence of any organic solvents.

17. A method according to any one of the preceding claims, in which stage (a) is carried out in the presence of a polymerisation inhibitor for the conjugated diene or triene.

18. A method according to Claim 17, in which the polymerisation inhibitor is a copper salt of a fatty acid.

19. A method according to Claim 17 or 18, in which the polymerisation inhibitor is copper stearate, copper oleate, copper 2–ethyl–hexoate or copper napthanate.

20. A method according to Claim 17, in which the polymerisation inhibitor is a N-substituted aryl compound.

21. A method according to Claim 17 or 20, in which the polymerisation inhibitor is 1,2–dinitrobenzene.

22. A method according to any one of the preceding claims, in which the solvent used in stage (b) is a chloro-substituted alkyl, aryl, alkaryl or aralkyl compound.

23. A method according to Claim 22, in which the solvent is dichloromethane.

24. A method according to any one of the preceding claims, in which the nucleophile is a straight or branched chain monohydric alcohol having

up to 8 carbon atoms, a straight or branched chain dihydric alcohol having up to 12 carbon atoms, ethylene oxide, propylene oxide, phenol, a substituted phenol, a mono-amine, a diamine, a thiol or a di-thiol.

25. A method according to Claim 24 in which the nucleophile is methanol.

26. A method according to any one of the preceding claims, in which the nucleophile is added to the reaction intermediate in stage (b) at a temperature of from -15°C to -5°C.

27. A method according to Claim 26, in which the temperature is about -10°C.

28. A method according to any one of the preceding claims, in which, following the addition of the nucleophile in stage (b), further reaction is carried out at ambient temperature.

29. A method according to any one of the preceding claims, in which stage (b) is carried out under acidic conditions.

30. A method for the production of a phospholene oxide, substantially as herein before described with reference to any one of the Examples.

31. A phospholene oxide produced by the method of any one of the preceding claims.

32. The use of a phospholene oxide according to Claim 31 as a flame retardant for a polymeric material and or as a wetting agent.

33. A flame retardant polymeric material according to Claim 32 which is a polyurethane.

Improved Synthesis of 1-Methoxy-3-methyl-2-phospholene Oxide Utilising Multivariate Optimization Analysis

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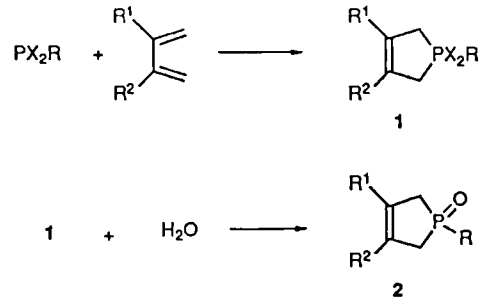
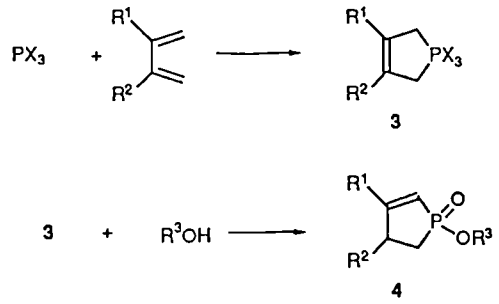
The synthesis of 1-methoxy-3-methyl-2-phospholene oxide from 1,1,1-trichloro-3-methyl-3-phospholene initially gave low yields of around 25%. Attempts to optimise the yield by classic traditional methods, that is, changing only one variable at a time (OVAT) resulted in no significant improvement in the yield. Using multivariate optimization techniques, the yield was rapidly and significantly improved to around 90%. Data was also gathered on the significant variables and the important variable interactions.

Most literature[1-6] concerned with the synthesis of phospholene oxides[2] follows a reaction scheme involving an alkyl phosphorus dihalide and a diene (Scheme 1). This paper refers to a slightly different synthesis which yields an ester (Scheme 2).



Scheme 1 Where X represents halide atoms and R is an organic side chain.



Scheme 2

The desired 1,1,1-trichloro-3-methyl-3-phospholene (Scheme 2; 3 where X = Cl, R^1 = Me, R^2 = H) was prepared from phosphorus trichloride and isoprene by heating the two reactants to 50 °C for 20 h under a gently flowing atmosphere of nitrogen. This gave an 80% yield similar to yields previously reported,[1,2,7,8] but in a fraction of the time, *i.e.* 20 h not 20 days. This is attributed to the reaction being conducted at 50 °C and not ambient temperature, as was the case with earlier workers. 1,1,1-Trichloro-3-methyl-3-phospholene was then reacted with methanol[9] to produce 1-methoxy-3-methyl-2-phospholene oxide (R^1 = R^3 = Me, R^2 = H) in 25% yield.

Attempts to increase this yield further by changing one variable at a time gave no significant improvement in the yield. The reaction is obviously dependent on a number of different variables which are almost surely interactive rather than independent. Therefore, procedures that make it possible to consider the joint influences of all variables simultaneously needed to be applied. Such multivariate techniques are available[10-12] and are in common use in industrial situations, but are rarely applied to fundamental research problems. Rigorous multivariate optimization requires a full factorial analysis, wherein the response of the reaction to all variables is probed. A fractional factorial design would do the job as well. Surprisingly it is necessary to include more factors in a fractional design to make it easier to avoid confounding a main effect with a two-factor interaction. At this early stage of the optimisation, it was deemed vital to investigate fully just three potentially significant variables to develop a firm understanding of these critical variables before progressing to investigate further variables. To use this technique, firstly one assesses the variables governing the experiment and decides which of them is likely to be significant. For this particular reaction, reaction temperature, concentration of 1,1,1-trichloro-3-methyl-3-phospholene 3 (X = Cl, R^1 = Me, R^2 = H) and addition time of methanol were selected. Pre- and post-mixing times, temperature for pre- and post-mixing, solvent choice, and concentration of methanol, were other variables which were considered. However, they were initially deemed less important, and it is helpful to minimise the number of variables to begin with so as to reduce the complexity of interpreting the results. A high and low value for each variable is then chosen giving eight different experimental conditions with the three selected variables at high and low levels (2^3 = 8). It is essential that the experiments are performed in a random order. This is necessary, as it is important, for example, not to investigate all the high temperature reactions of a set first and all the lower ones later. If this is done, a change caused by, for example, deterioration of reagent in storage may be ascribed to temperature change. The raw data (in this case percentage yield) is then processed in a pre-specified order. Owing to the design of the experiments four estimates of the effects of variables and variable interaction effects are produced.

Results and Discussion

Prior to using chemometric techniques to optimise the yield, the experiment consisted of slowly adding a known quantity of methanol to a known quantity of 1,1,1-trichloro-3-methyl-3-phospholene 3 (X = Cl, R^1 = Me, R^2 = H) in dichloromethane held at sub-ambient temperature. The mixture was then stirred until ambient temperature was attained and then neutralised with aqueous sodium carbonate solution and the product extracted with dichloromethane.

In applying chemometric techniques, firstly the variables to be investigated are selected. As mentioned previously it was

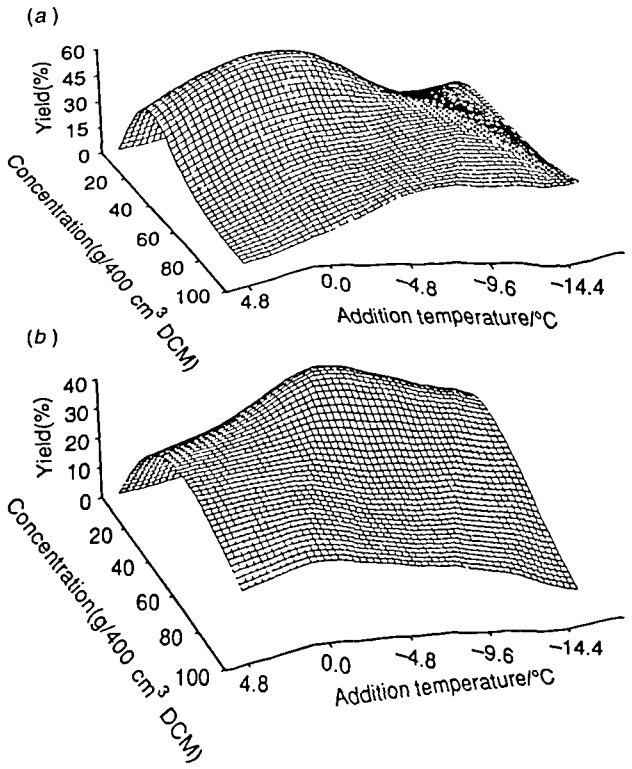


Fig. 1 Three-dimensional response surfaces based on data obtained in full factorial analysis: (*a*) low addition time; (*b*) high addition time

decided to investigate the effects of three variables. The three variables selected for the multivariate analysis were:

A = Addition temperature, −15 °C or 0 °C;
B = Concentration of 1,1,1-trichloro-3-methyl-3-phospholene, 50 g in 400 cm^3 of dichloromethane or 100 g in 400 cm^3 of dichloromethane;
C = Addition time of methanol, 1 h or 4 h.

The highest yield from these experiments was 42.5%, compared to previous yields of around 25%. Information on the importance of variables and variable interactions was also obtained. The effect of concentration of 1,1,1-trichloro-3-methyl-3-phospholene was highly significant and needed to be lowered. The addition temperature/concentration interaction was important, implying that increasing the addition temperature whilst lowering the concentration will increase the yield. Consequently the addition temperature needed to be increased slightly. The three-fold interaction was also found to be important, although normally three-fold interactions are negligible. It is difficult to draw any conclusions from the three-fold interaction as it is very difficult to visualise the effect of changing the addition temperature on varying concentration and addition time in a physical sense.

Having identified effects within the chosen parameters a few probing experiments outside of these could then be attempted to confirm initial findings, before attempting the new experiments dictated by the primary experimental investigations. The variable A was raised to 0 °C, B was halved to 25 g of 1,1,1-trichloro-3-methyl-3-phospholene in 400 cm^3 of dichloromethane and C was reduced to 30 min. The recorded yield was 57%, a good increase over the previous highest yield of 42.5%. Three more probing experiments were then performed, with only one variable altered, two with their addition temperatures at +5 °C and −5 °C and one with the stirring time halved to 1 h. In a sense this is a return to the classical research approach, however, one can measure the effect on the response when one factor is varied while the others are held at their optimum levels. This 'fine tuning' technique checks that the optimum has been located accurately for the variable chosen. These experiments gave yields of 42%, 51% and 54% respectively. All but the last of these probing experiments had been designed using evolutionary operations (EVOPS) techniques,[10] but could only incorporate variables previously studied. An indication of the complex variation of yield with the three variables studied is provided by the three-dimensional response surfaces presented in Fig. 1. These show that the highest yield obtained was about 57%, *i.e.* the summit on the low-addition-time surface. In an attempt to increase the yield, further variables were investigated. The new variables selected were concentration of methanol, stirring time and stirring temperature. Now a standard 2^3 experimental design could have been attempted with these variables, the original variables studied being held constant at pre-specified levels. However, it was felt that the interaction effects between 'new' and 'old' variables would be significant and that a study of these would also yield more valuable information on the mechanism of the reaction as well as being time saving. With five variables (fixing the concentration of 1,1,1-trichloro-3-methyl-3-phospholene at 25 g in 400 cm^3 of dichloromethane), 32 experiments (2^5) need to be performed to complete a full factorial analysis. However, by dividing the 32 experiments into four separate blocks of eight experiments, fractional factorial experimental designs[10] may be performed. The principal block is carefully designed to include those variables and variable interactions which are thought to be the most important. If the design is correct then the significant variables and variable interactions will be identified by strong responses. In this manner the proposed important variables and variable interactions are examined efficiently. However, one must also be aware of the fact that these strong responses generated by performing only the principal block will be aliased with certain two-factor interactions. Thus a strong response is associated with two factors, either or both of which may have significance. A good design chooses the appropriate aliases to be examined and thus overcomes the disadvantage that some of the effects are confounded by one another. If it is unclear which of the two factors is significant then further blocks must be performed to clarify the situation.

The highest yield attained from the principal block was 78%. The important variables were found to be the addition temperature (A)/stirring temperature (E) interaction and the methanol concentration and/or the effects with which they are aliased. The addition temperature/stirring temperature interaction, which is aliased with the methanol concentration/stirring time interaction, should be increased. That is, the yield will be increased by lowering the addition temperature and subsequently raising the stirring temperature. It was unclear whether the methanol concentration effect was important or not and so other experiments were performed to ascertain this using simplex EVOPS analysis. From these it was established that the concentration of methanol was of little importance but the two-factor interaction of addition time of methanol with stirring temperature with which it was aliased was of significance. It therefore follows that if the stirring temperature is raised then the methanol addition time must consequently be reduced in order to increase the interaction effect. Initially a yield of 83.5% was obtained with a further experiment leading to a 90% yield. Repeated experiments now have yields of 90 ± 3%. Further yield improvement towards 100% was thought to be too time consuming to investigate and perhaps, in real terms, unobtainable. While these optimum synthesis conditions may only hold for methanol, the information gathered on variable interactions and their significance on yield should be very useful in achieving optimum yields of all esterification reactions of this type.

Table 1 Responses from full factorial design

Order	Treatment combination	Response (% yield)
3	(1)[a]	24.8
6	a	42.5
1	b	39.0
7	ab	18.2
2	c	32.8
4	ac	33.0
8	bc	13.2
5	abc	24.3

[a] Indicates low A, low B, low C.

Table 2 Yates analysis of responses from initial full factorial

Response	1	2	3
24.8	67.3	124.5	227.8
42.5	57.2	103.3	$8.2 = 4\,eff_a$
39.0	65.8	−3.1	$-38.4 = 4\,eff_b$
18.2	37.5	11.3	$-27.6 = 4\,eff_{ab}$
32.8	17.7	−10.1	$-21.2 = 4\,eff_c$
33.0	−20.8	−28.3	$14.4 = 4\,eff_{ac}$
13.2	0.2	−38.5	$18.2 = 4\,eff_{bc}$
24.3	11.1	10.9	$49.4 = 4eff_{abc}$

Experimental

Instruments.—All infrared spectra were obtained using a Perkin-Elmer 1710 FTIR with the sample in the form of a film. NMR spectra were taken on a Bruker A.C. 300 MHz NMR using $CDCl_3$ solvent. *J*-Values are in Hz. Combined GC/MS analyses were performed using a Varian 3400 GC coupled to a Finnigan 4500 MS. Samples were injected into the GC as solutions in dichloromethane.

Optimum Procedure for Synthesis of 1-*Methoxy*-3-*methyl*-2-*phospholene Oxide.*—To a mixture of isoprene (330 cm^3) and copper stearate (1 g) was slowly added phosphorus trichloride (260 cm^3) under an atmosphere of gently flowing nitrogen. The mixture was then heated to 50 °C for 20 h. The solid product obtained was washed with light petroleum (b.p. 40–60 °C). To dichloromethane (400 cm^3) was added 1,1,1-trichloro-3-methyl-3-phospholene (25 g; 0.125 mol) and the mixture stirred at −10 °C under a flowing atmosphere of nitrogen. Distilled methanol (136 cm^3; 13 mol) was then added over 15 min the temperature being kept at −10 °C, then it was stirred at room temperature for 1 h. The solution was then neutralised with saturated aqueous sodium hydrogencarbonate. The dichloromethane layer was separated and the aqueous layer extracted with dichloromethane (5 × 200 cm^3). The organic layers were combined and the solvent removed under reduced pressure, leaving a dark red oil of 90% yield, b.p. 75–79 °C at ambient pressure; ν_{max}/(film)/cm^{-1} 1615, 2850 and 2900; δ_H(270 MHz) 1.95 (5 H, m, Me and CH_2), 2.48 (2 H, d, *J* 42.76, CH_2), 3.72 (3 H, d, *J* 11.24, OMe) and 5.80 (1 H, d, *J* 22.66, CH); δ_C(67.8 MHz) 21.0 (q, Me), 22.6 (s, CH_2P), 31.1 (t, CH_2), 53.3 (q, OMe) 116.2 (d, CHP) and 164.2 (d, CHMe); δ_P(36.1 MHz) 76.41; *m*/*z* (EI) (GC MS) 147 [(M + H)$^+$], 116 [(M + H)$^+$] − Ome; *m* *z* (CI) (GC/MS) 293 [(Dimer + H)$^+$] and 147 [(M + H)$^+$].

Optimization of the Synthesis of 1-*Methoxy*-3-*methyl*-2-*phospholene Oxide.*—The optimization procedure employed was completed in the following manner. At first a series of eight experiments (2^3 full factorial design) were run with the three pre-specified variables set at high and low levels, the responses, in this case percentage yields, being recorded as shown in Table 1. Each individual experiment is known as a treatment combination and is expressed in shorthand note form. If the lower case letter of the assigned variable is present it infers that the variable is at its high value, if it is absent, the variable is at its low value. Hence ac means high A, low B, high C.

Table 3 Fractional factorial analysis

Treatment combination	Response (% yield)	Effect	Aliasing effect
(1)	45.1		
ad	60.2	−2.85	A with −BD
bde	62.5	0.2	B with −CE + AD
abe	46.8	3.6	D with −AB
ce	77.8	9.35	C with −BE
acde	49.8	−2.55	AC with −DE
bcd	53.6	−1.8	E with −BC
abc	70.8	19.0	AE with CD

The variables, with their high and low values were as follows: variable A—addition temperature, low −15 °C, high 0 °C; variable B—concentration of 1,1,1-trichloro-3-methyl-3-phospholene, low 50 g in 400 cm^3 of dichloromethane, high 100 g in 400 cm^3 of dichloromethane; variable C—addition time of methanol, low 1 h, high 4 h. In all of these experiments after the addition of 68 cm^3 of methanol over the desired addition time, the mixture was stirred for a further 2 h whilst being brought to ambient temperature. It was then neutralised with aqueous sodium hydrogencarbonate and extracted with dichloromethane. A rapid and simple method of calculating the effects in factorial design is Yates' algorithm [10] which is applicable to both complete and fractional factorial designs. Yates' algorithm was applied to the responses shown in the standard format in Table 1. These responses were then treated in successive pairs as shown in Table 2.

The first four entries in column 1 of Table 2 were obtained by adding the pairs of responses together (*i.e.* 24.8 + 42.5 = 67.3 *etc.*). The lowest four numbers in column 1 were obtained by subtracting the top number of each pair from the lower number (*i.e.* 42.5 − 24.8 = 17.7, *etc.*). Column 2 is then obtained in the same way as was column 1. This was then repeated to obtain column 3 from column 2. Column 3 represents the results of the Yates' analysis. The first number is equal to the total of all the responses and is used as a check that the calculations have been executed correctly. The remaining numbers are equal to each of the effects examined multiplied by four, *i.e.* half the number of experiments performed. Thus the effects of the variables investigated (*i.e.* temperature, concentration and time) together with their interaction effects can be evaluated as follows:

Effect of addition temperature (variable A) = 2.05
Effect of concentration (variable B) = −9.6
Effect of addition time (variable C) = −5.3

Interaction Effects

Effect of A on B on C = 12.35
Effect of A on C = 3.6
Effect of A on B = −6.9
Effect of B on C = 4.55

Using a probability plot it was seen that concentration, the two-fold interaction of addition temperature on concentration and the three-fold interaction were all significant. Following multivariate simplex EVOPs designs a new treatment combination (probing experiment) was produced by selecting the four treatment combinations that gave the best responses, rejecting the worst of these and then calculating the new treatment combination. This is also moderated by the variable effects generated, *i.e.* since concentration effect is negative then concentration should be lowered and addition temperature increased to allow for the two-factor interaction effect of addition temperature on concentration. The addition time

Table 4

Addition temperature/ °C	Concentration of 1,1,1-trichloro-3-methyl-3-phospholene (g in 400 cm^3)	Addition time of methanol/ h	Concentration of methanol/ cm^3	Stirring time/ h	Stirring temperature[a]/ °C	Yield (%)
−15	50	1	68	2	RT[b]	25
0	50	1	68	2	RT[b]	42
0	25	0.5	136	2	RT[b]	57
−10	25	0.25	272	0.5	RT	78
−10	25	0.5	136	2	−10	83
−10	25	0.25	136	0.5	RT	90
−10	25	0.25	136	1	RT	95

[a] RT is ambient. [b] Indicates mixture stirred for 2 h whilst reaching RT, *i.e.* not stirred at RT for 2 h.

should also be reduced. The three-fold interaction is very difficult to interpret, as mentioned earlier. The new probing experiment generated had the variables set at the levels: addition temperature 0 °C; concentration of 1,1,1-trichloro-3-methyl-3-phospholene, 25 g in 400 cm^3 of dichloromethane; 136 cm^3 of methanol added over 30 min. The remainder of the experiment was as before. The yield was recorded as 57%, a significant increase over the previous highest yield of 42.5%. The multivariate simplex EVOPs exercise was used to generate sequentially three more experiments, with only one variable changed, two with the temperatures of +5 °C and −5 °C and one with the stirring time halved to 1 h. These experiments gave yields of 42%, 51% and 54% respectively, all lower than the 57% level achieved above.

This suggested that other factors were also significantly affecting the yield and needed to be investigated. Five variables were selected and a fractional factorial analysis performed to reduce the number of experiments needed to produce the required information. The primary block is shown in Table 3, the variables defined being: Variable A, addition temperature, low: −10 °C, high: 0 °C; Variable B, addition time of methanol, low: 15 min, high: 30 min; Variable C, concentration of methanol, low: 136 cm^3, high: 272 cm^3; Variable D, stirring time, low: 30 min, high: 2 h; variable E, stirring temperature, low: addition temperature, *i.e.* no change, high: ambient temperature. As mentioned each effect will be aliased with a two-factor interaction which may or may not be significant.

Effects calculated *via* Yates' analysises [10] are:

Effect of addition temperature = −2.85 (aliased with addition time of methanol/stirring time interaction).

Effect of addition time = 0.2 (aliased with concentration of methanol/stirring temperature interaction and addition temperature/stirring time interaction).

Effect of stirring time = 3.6 (aliased with addition temperature/addition time of methanol interaction).

Effect of methanol concentration = 9.35 (aliased with addition time of methanol/stirring temperature interaction).

Effect of addition temperature/methanol concentration interaction = −2.55 (aliased with stirring time/stirring temperature interactions).

Effect of stirring temperature = −1.8 (aliased with addition time of methanol/concentration of methanol interaction).

Effect of addition temperature/stirring temperature interaction = 19.0 (aliased with methanol concentration/stirring time interaction).

The largest effect is due to the addition temperature/stirring temperature interaction, next is the addition time of methanol/stirring temperature interaction and not the methanol concentration with which it is aliased. The latter observation arose from further probing experiments conducted within the set levels of the chosen variables. Using the treatment combination notation, experiment abcd gave a yield of 70%, experiment bc gave a yield of 62%, experiment bd gave a yield of 83.5% and experiment e gave a yield of 90%. On repetition of the latter experiment, yields of 90 ± 3% were recorded. By lengthening the stirring time to 1 h a yield of 95% has been achieved.

Conclusions

Excluding duplications, a total of 28 experiments each having a defined set of fixed variables were completed and the yield of 1-methoxy-3-methyl-2-phospholene oxide was increased from 25% to around 90%. Table 4 shows the changes to those variables giving the best yields after each new approach.

The improvement of the yield to over 90% was only achieved by simultaneous variation of the factors. It was found to be impossible to increase the yield above 25% by varying the individual factors in the classical manner. This clearly shows the power of optimisation by multivariate analysis in the case of syntheses in which multi-parameter interactions are significant.

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References

1 U. Hasseroot, K. Hunger and F. Korte, *Tetrahedron*, 1963, **19**, 1563.
2 K. Hunger, U. Hasseroot and F. Korte, *Tetrahedron*, 1964, **20**, 1593.
3 L. D. Quin, J. P. Gratz and T. P. Barket, *J. Org. Chem.*, 1968, **33**, 1034.
4 K. Moedritzer, Can. Pat., 958, 145/1974 (*Chem. Abstr.*, 1975, **82**, 112443w).
5 D. K. Myers and L. D. Quin, *J. Org. Chem.*, 1971, **36**, 1285.
6 A. O. Vizel, V. K. Krupnov, B. A. Arbuzov and L. M. Fadeeva, *Zh. Obshch. Khim.*, 1971, **43**, 2128.
7 M. A. Harthcock, *J. Phys. Chem.*, 1984, **88**, 1365.
8 R. G. Nelb and K. G. Saunders, U.S. Pat. 4,738,990/1988 (*Chem. Abstr.*, 1990, **109**, 56222k).
9 H. Weitkamp and F. Korte, *Z. Anal. Chem.*, 1904, **204**, 245.
10 G. E. P. Box, *Statistics for Experimenters*, Wiley, New York, 1978.
11 R. Carlson, *Chem. Scripta*, 1987, **27**, 545.
12 E. Morgan, *Chemometrics: Experimental Design*, J. Wiley, Chichester, 1991.

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